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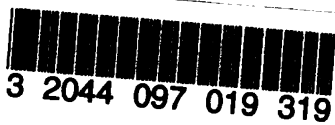
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° ELEMENTS
OF
CHEMISTRY

BY
RUFUS P. WILLIAMS

*In charge of the Chemical Department of the English High School,
Boston, and Author of "Introduction to Chemical Science,"
"Chemical Experiments, General and Analytical," and
"Laboratory Manual of Inorganic Chemistry"*

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1898



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PREFACE.

To the average young person Chemistry is the most fascinating of sciences. Its experiments teem with newness; odorous gases, colored liquids, and precipitates stimulate the powers of observation, and explosions fill his mind with wonder. Everything will end there unless the superficial love of observation leads to the deeper love of explanation. Here is the function of the text-book and the teacher. The subject must be rightly presented; the pupil must be helped *to think scientifically*.

The author has worked with two ideas in mind: (1) To treat the subject accurately and clearly, (2) to make it have a real fascination for the student. On these two ideas hangs the law of scientific progress of students. The semi-popular introduction to various subjects, as well as statistical matter and many graphic illustrations, find here their *raison d'être*.

The methods of the book are the result of the author's experience and personal contact with some twenty-five hundred pupils in chemistry. Many topics—such, for example, as Valence, Union by Volume, Laws of Combination, etc.—have been treated in quite an original manner, and, it is hoped, one that will be found clear to an un-

usual degree. Although the "Introduction to Chemical Science," issued nearly ten years ago, has each year to the present time met with an increased demand, yet the author has seen fit to follow the *inductive system* less vigorously in the present book, and all topics have been treated with greater fullness than in the previous one, since, for study and reference, students should have a book which gives all needed information of what is known on the subject in hand. They should study a question as a business man would examine an investment, looking at it from every point of view—the only method which can give the best mental training.

The brief historical treatment of elements, theories, and laws places the student *en rapport* with the great names and science-building periods of chemistry. It is not necessary—hardly even desirable, perhaps—that exact dates be memorized.

In the descriptive portions, paramount importance—as seems proper—is given to chemical properties. More space than is usual has been devoted to the discussion of laws, theories, and general principles, since a perfectly clear understanding can be obtained in no other way, and a half idea is usually worse than none at all. Exercises and problems, following these discussions, have the same end in view.

A much larger number of experiments is inserted than it is expected will be made use of either in lecture room or laboratory. This enables the instructor to make a selection, beside which the mere reading of an experiment

is useful to the student. Minute details and suggestions are usually omitted, since most students now use a laboratory note-book with ampler directions.

Rare elements and unimportant compounds have for the most part been omitted. The modern spelling and pronunciation of chemical terms have been adopted, as recommended by the American Association for the Advancement of Science.

The division of matter into coarse and fine print enables a choice to be made in schools which have time for only a portion of the text; still the fine print does not necessarily indicate matter of small importance, and if classes cannot satisfactorily complete the entire book, it is recommended that they go no further, for example, than through the non-metals.

The question is often asked: What proportion of time should be allotted to the laboratory, and what to recitation? After some careful but heroic experiments on a large scale, the author is firmly of opinion that in ordinary schools, with three to five hours per week for chemistry, not over half of the time—less if anything—should be spent in the laboratory. Brilliant students may profitably spend a larger proportion of time, but the average beginner will, in that case, learn mechanical manipulation mostly, and soon lose his interest. With one-third laboratory work, supplemented by well-chosen lecture-room experiments, and somewhat more than half the time devoted to recitation and explanation, the author has yet to find any classes lacking in enthusiastic interest.

For facts, theories, and experiments the author is indebted to authorities too numerous to mention, but a few choice reference books are named in the Appendix. Most of the drawings for the illustrations—which tell their story so well and with such accuracy of detail—were made by Mrs. Lillian W. Williams. To Dr. S. P. Mulliken of the Massachusetts Institute of Technology, formerly Director of Chemistry in Clark University, for critical and painstaking reading of the manuscript, the author wishes to express his thanks in a particular manner. He is also under great obligation to Dr. J. E. Sanborn of Melrose, Mass., for careful criticism of the English. But for all errors and shortcomings, of whatever nature, the author assumes entire responsibility, trusting to a criticism friendly rather to education than to cynicism.

CAMBRIDGE, MASS.,

June, 1897.

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ELEMENTS OF CHEMISTRY.



CHAPTER I.

THE PROVINCE OF CHEMISTRY.

1. *Matter is anything which occupies space, which we can see or feel, or which has weight.* Any one kind of matter is known as a *substance*. The particles of which any substance is composed are in constant motion, and the forms of matter have many different motions, each produced by some form of *energy*. *Chemistry* has to do with matter and energy, and so has *Physics*. We must at the outset learn to distinguish between physical changes and chemical changes, in order to understand the province of chemistry.

2. **History.**—The history of chemistry may be divided into three periods: (1) The period of Alchemy, from the earliest Egyptian or Arabic times to the middle of the seventeenth century. The attempt to change metals into gold and the search for the elixir of life were the chief aims of the experimenter. This included the iatro-chemical period, or age of medical chemistry. (2) The Phlogiston period, from the close of the Alchemical age to the end of the eighteenth century. Chemical changes were attributed to a very subtle principle called phlogiston, and fire showed the escape of phlogiston. Becher and Stahl were the founders of this theory. (3) The Scientific period, ushered in near the close of the eighteenth century. Lavoisier, a French chemist, was the originator of the present ideas of combustion and chemical union, and thus the founder of scientific chemistry.

3. Physical and Chemical Changes. — We distinguish two great classes of changes in matter, physical and chemical. The former are the more superficial, and leave the substance in its essence and main properties about the same as before the change. The latter affect the nature of the substance, giving new forms of matter with different properties. We shall begin our study of matter by breaking it up physically and then chemically, and noting whether its properties are changed.

4. Physical Division. — There are two common ways of dividing matter physically, (1) by crushing or cutting, (2) by solution. Sugar is a substance by which we may illustrate both methods. Its crystals can be broken up into fine particles, and still they will retain the same sweet taste, white color, and — examined under the microscope — the same crystalline structure. It is sugar still, and hence the change is physical. Sugar can be dissolved in water and yet will retain its sweetness, and by slow evaporation of the water we can once more obtain the crystals. Here again the essence of the substance has not been altered. These processes have merely broken up the sugar into finer particles and mingled them with those of the water.

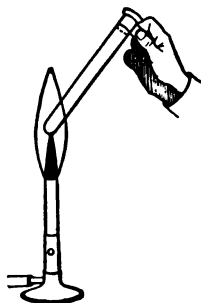


FIG. 1.

Exp. 1. — Examine a few crystals of sugar, notice their color and taste, then crush or grind some, taste the powder and examine with a lens or microscope. Its particles still have sensible size, and are white and sweet as before. What sort of change would this indicate?

Exp. 2.—Put about 5^g of sugar into a clean test tube and cover it with water (about 5^{cc}). Hold the tube in a Bunsen flame (Fig. 1) until the liquid boils and the sugar dissolves. Cool the liquid—hold the tube under a jet of water—and taste a drop. The sugar has been very finely divided and the particles intermingled with the water particles. This is called a *solution*; the sugar is said to be *soluble* in water, and water is a *solvent* of sugar. Is this a physical or a chemical change, and why? See whether you can separate the sugar from the water by pouring it on a filter paper in a funnel and catching what runs through—called the *filtrate*—in a clean test tube (Fig. 2).

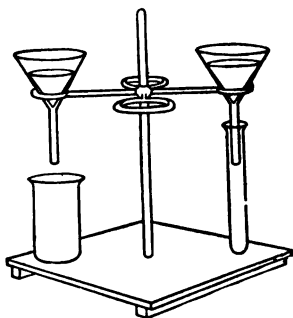


FIG. 2.

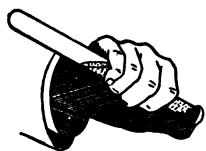


FIG. 3.

If anything is left on the paper it is called a *residue*. See whether there is a residue and whether the filtrate is sweet. Does it indicate that substances in solution do or do not go through the filter? Pour half of the filtrate into another tube—for use in Exp. 3. To the other half add an equal volume of water, shake the tube (Fig. 3), then taste a drop and compare it with the previous solution. In which is the sugar more finely divided? Finally, add more water, shake it, and taste again.

5. Limit of Divisibility.—The more we dilute the sugar solution the more finely we suppose the sugar particles to be divided, as a drop from any part of the solution is equally sweet, but is less so than before dilution. It is an interesting question whether it would be possible to go on dividing the sugar forever; if, *e.g.*, we throw into the ocean a crystal of it, would this continue to subdivide till every part of the sea contained some portion of it? A solution of the red pigment fuchsin, .00000002^g in 1^{cc} of alcohol, gives a distinct color. Such experiments would seem to indicate that there is no limit to

the divisibility of matter. But other considerations lead to the belief that such a limit does exist, that there is a *smallest particle* of sugar and of every other substance. These particles are supposed to be incapable of further division except by chemical means, and then they give rise to other forms of matter. To these smallest particles is given the name *molecules*. Molecules in general are thought to have most of the properties which larger particles of the same substance possess, and to be acted upon in similar ways, except that they cannot be further divided by physical means. In fact, masses of matter are made up of aggregates of molecules.

6. Chemical Division. — Although by solution we may reach the limit to which sugar can be divided by physical agencies, yet we may break it up chemically either (1) by heat, or (2) by some reagent, as sulfuric acid. In each of the last cases, substances are made, having different properties from sugar (*i.e.*, different color, taste, form, etc.). It is no longer sugar, a chemical change having taken place. All forms of matter can be acted upon by some reagent or

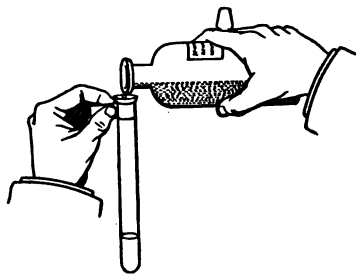


FIG. 4.

other, or by heat or electricity, and new forms produced. Such changes sometimes result in breaking up matter into simpler forms, at others in building up more complex forms.

Exp. 3. — Into the other half of the sugar solution from Exp. 2 slowly pour sulfuric acid (Fig. 4). Observe the change of color, temperature of the tube, the expansion of the contents, the odor therefrom, and

the change from a liquid to a solid. All these phenomena seem to indicate a chemical change. Instead of sugar there is a black substance resembling charcoal. The sulfuric acid added is here called a *reagent*. *A reagent is a substance which produces a reaction. A reaction is a chemical change.* The explanation of this particular reaction is that the acid has great affinity for water. *Affinity is chemical attraction which tends to form new combinations of elements.* Now the affinity for water is one of the properties of sulfuric acid. The acid first combines with the solvent water, then — if the solution is strong — it breaks up the sugar into its constituents, giving carbon and water and some gaseous products. It unites with the water and sets the carbon free in the solid state. The chemical action generated much heat, and the gases escaped and caused the mass to rise. Carbon is very porous, and it absorbed into its pores the acid and water. The compound of acid and water is called simply dilute sulfuric acid.



FIG. 5.

Exp. 4. — Heat a few crystals of sugar in an evaporating dish over a Bunsen flame (Fig. 5), noting all effects.

7. Elements. — The sulfuric acid broke up the sugar so as to give carbon and water, and of course decomposed its smallest particles, the molecules, in the same way. Hence the molecule — which is the smallest particle of sugar — is a compound substance, and is therefore made up of other molecules. But are carbon and water compound bodies? Could we by chemical reagents or heat continue to split up *their* molecules into still other forms of matter? There are certain substances which chemists are not able, by any known means, to break up into other kinds of matter. These they have named *elements*. There are some seventy-five or more of them, the exact number being in doubt, and new ones being discovered from time to time. Not over half of them are of interest to the student of general chemistry. The others are rarely met with. In Lavoisier's time only twenty-three were known.

From this small number of elements are built up all the compounds — amounting to tens of thousands — that are found in nature or made in the laboratory.

Copper is an element because we cannot obtain from it anything but copper, without causing something to unite with it. Copper oxid or copper sulfid can be made from it, but those are compounds formed by the union of other elements with copper. An element is, therefore, matter that cannot be divided by chemical agencies. A list of the common elements is given in Chap. II, the most important being in heavy type. The Appendix contains a complete list.

8. Molecules and Atoms. — *A molecule is the smallest particle of an element or a compound which exists alone and retains most of the properties of the mass of the substance.* There are two classes of molecules, elementary and compound. We find reasons for supposing that molecules of elements can be broken up into still finer particles which are called *atoms*. It is impossible to divide or break up an atom by any means known, either physical or chemical. Atoms are the final divisions of all elements, and may be called the unit in chemistry. But atoms as a general rule do not exist separately or uncombined, the molecule being the smallest particle which exists alone (except in a few cases in which atoms and molecules are identical, Chap. XXVII).

Molecules of elements are composed of atoms of the same kind of matter. Those of compounds have atoms of different kinds. There are as many kinds of atoms as of elements. An atom is the smallest particle of a substance, and it exists not alone, but combined with other atoms to form molecules.

An atom of hydrogen is the smallest particle of hydrogen that exists in combination with other atoms to form a molecule. Molecules of elements usually have two atoms each. Those of compounds may have any number from two to hundreds, but the number is always the same for a given compound. The molecule of common salt always has two atoms, that of water three. The breaking up of molecules of compounds into atoms is a sort of *analysis*. These atoms may unite to form compounds, — a process called *synthesis*, — as when charcoal burns. Finally, by putting together two compounds the atoms often change places and two new compounds are formed — a process known as *metathesis*, or *double decomposition*; as when solutions of silver nitrate and sodium chlorid are mixed they become silver chlorid and sodium nitrate.

Exp. 5. — Mix on paper about equal bulks of iron filings and fine sulfur. Draw a magnet along the under side of the paper, and notice that the iron can be separated from the sulfur. This is now a *mixture* without any chemical affinity between the two elements. Put the mixture into an ignition tube and heat it (Fig. 6), noting any red glow, which should spread through the whole mass, and which indicates that a chemical change has taken place. Break the hot tube with a jet of water and examine the contents, noting color, lustre, form, kinds of substances, etc. The explanation is that the iron and sulfur have united to form a compound substance called iron (or ferrous) sulfid, which has different properties from either the iron or the sulfur. *Compounds usually have very different properties from the elements of which they are composed. Mixtures are not held together by affinity, and can be made in any proportion — in which they differ from compounds.*

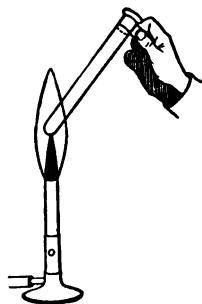


FIG. 6.

Perform the same experiment as above, using, however, copper filings or turnings instead of iron. These two experiments illustrate *synthesis*.

9. Chemical Changes. — If a piece of platinum wire is held in the outer part of a Bunsen flame, it becomes red hot, glows, and expands, but on removing it the platinum is found unchanged. If, however, a piece of wood is held in the flame, it not only glows, but takes fire and burns to an invisible gas, leaving a very little ash or a piece of charcoal. The burning wood illustrates a chemical change — the combination of elements; the glowing wire, merely a physical one. Iron can be magnetized, and still its main properties are unchanged. If it rusts, it is no longer iron, but a compound of it.

Exercises. — Are the following cases illustrations of physical, or chemical changes? The falling of rain, the burning of sulfur, the explosion of gunpowder, the souring of milk, the radiation of heat, the evaporation of water, the decay of vegetation, the breaking of iron, the bleaching of cloth, the fermentation of apple juice, the crystallization of salt from solution, the digestion of food. The following experiments illustrate changes. Ascertain whether they are physical or chemical.

Exp. 6. — To a solution of copper chlorid in a test tube add a little ammonium hydrate, and note the effect.

Exp. 7. — Add to a solution of lead nitrate a few drops of sulfuric acid. A white solid is formed, which is insoluble in the liquid, settles to the bottom, and is called a precipitate.

Exp. 8. — To a solution of mercuric chlorid add a solution of potassium iodid. The last three experiments are instances of double decomposition. They also show chemical action by direct contact, without the aid of heat.














Exp. 9. — Put into a small test tube 4 or 5 crystals of lead nitrate and heat it a moment in a Bunsen flame.





10. Chemical Affinity. — It is evident that some force must exist to bind atoms together so as to form molecules, or to hold elements in combination, and thus form compounds. This force is called *chemical affinity* or *chemism*. The compound is very different from the elements of which it is made up, the molecule from its atoms, as a

word differs from the letters it contains. Chemical affinity has taken away the old properties from the elements and impressed new ones upon the compounds. The corresponding physical force which holds molecules together is called *cohesion*. *Chemical affinity may act between atoms of the same kind or of different kinds; it may be strong or weak, but it acts only at short distances.* It was easy to break up the attraction of the carbon for the other elements in sugar, but it is much more difficult to resolve water into its elements, — hydrogen and oxygen. Affinity is one of the agencies with which we have to deal in chemistry, but it may be assisted or counteracted in many ways, as by heat, electricity, or reagents. A reagent that will break up one compound will often form another. The same is true of different degrees of heat, of the electric current, and of mechanical forces. At very high temperatures compounds are often broken up. At extremely low ones reactions scarcely take place.

11. Physical Mixture.— When sugar dissolved in water the result was called a *mixture*. In the iron and sulfur experiment, before heat had caused the elements to unite in exact proportions, there was simply a mixture; but after the action, the two elements became a compound with new properties. In all cases where elements are not united in exact proportions, and where there is not the action of chemical affinity, the result is a mixture, not a compound. Elements or compounds may be mingled in any proportion and no new substances be formed, but the beginner should not put together chemicals ignorantly, or the attempt may be disastrous.

12. Properties. — A *substance* is any portion of either an element or a compound. The *properties* of a substance are the qualities which inhere in it and form a part of it. Properties are physiological, physical, chemical, etc. Physiological properties of a substance show its action on the human system, *e.g.*, sugar is sweet and chlorin is poisonous. Physical properties have reference to external appearance, as color, lustre, state, specific gravity. Chemical properties of a substance — to which especial attention will be given — are such as pertain to its affinity for other substances, its action in regard to combustion, etc., as the great affinity of carbon for oxygen, the inertness of nitrogen, and the solubility of zinc in hydrochloric acid.

13. Illustrations of Atoms and Molecules. — We do not know the size or the form of atoms or of molecules, since both are invisible even to the highest powers of the microscope. Liquids, when free, tend to assume the spherical form, and we may imagine atoms to be spherical also, as $\circ \bullet$. The spaces separating atoms are much greater than the atoms themselves. Lines drawn halfway between consecutive atoms of an element like hydrogen give a boundary and enclose what may be called the volume of the atom or the *atomic volume*. We may represent an atomic volume by a cube  or by a square , the former being more accurate, the latter more convenient. With the enclosed atom it would be  or . The *molecular volume* we picture by two cubes  or squares . By a law which we shall study a little later (Chap. XIX), molecular volumes are the same for all gases. Each is twice the hydrogen-atom volume — since there are two atoms in the hydrogen molecule . This hydrogen-atom volume we will now call an *atomic volume*. It is constant , and is half a molecular volume . We thus make the atomic volume  the unit of volumetric measurements. All molecular volumes are represented as twice that size, *viz.* , irrespective of the number of atoms they contain. Elements like oxygen, which have two atoms of the same kind to the molecule, may be figured ; compounds like common salt, with two different atoms, ; water, which has two of hydrogen and one of oxygen,

. Ammonia has one of nitrogen and three of hydrogen, as . Alcohol vapor has nine atoms to the molecule, and of course the atoms must be crowded much more closely than those of ammonia or water vapor, since they cannot be made smaller. Some organic molecules are supposed to have hundreds of atoms. A few elements have a single atom to the molecule, a few have four atoms (temperature and state varying somewhat the result), as mercury , and phosphorus . Atoms and molecules are usually represented in another way by symbols (Chap. II), but in order to understand and apply the laws on which chemistry is founded we must get a clear conception of the unit in volumetric measurements.

Chemistry may be defined as that science which treats of matter in its simplest forms, and of the various combinations of those forms.

CHAPTER II.

ELEMENTS AND COMPOUNDS.

14. *An element is a substance from which no other kind of matter has been obtained, except by union with some other substance.* From iron chemists have never been able to obtain anything but iron. It may unite with oxygen or chlorine and form compounds of the element, but only iron can be got out of it. *A compound is a substance made up of elements united together in exact and unvarying proportions by a force called chemical affinity.* Water is a compound of hydrogen and oxygen, united always in the same proportions by chemical affinity.

15. History. — The philosophers at the time of Aristotle and before believed in four elements, *earth, water, air, fire*, but their ideas of elements were different from ours. They thought every substance could be transformed into any other substance. Lavoisier first clearly defined an element, and classed the metals as elements. The theory of atoms had been held two thousand years, but Dalton in 1804 revived it, and made it the foundation of the chemical theory. Avogadro and Berzelius, 1811, first distinguished between atoms and molecules. The present symbols were first applied by Berzelius in 1813.

16. Atoms. — The present notion of atoms and molecules is something like this: An atom is extremely small, indivisible and unchangeable by either physical or chemical means; it has a definite weight, which is invariable for that element, and exhibits for other atoms an attractive force, or chemical affinity, which varies for different ele-

ments and under different conditions. This kind of attraction between atoms is operative only at very short distances.

17. Molecules. — A molecule is a group of atoms held together by chemical affinity. The molecules of a given substance always contain the same kind of atoms and the same number, but those of different substances have usually different kinds of atoms and varying numbers. In the same substance the strength of affinity between the atoms is the same; *e.g.*, a given temperature will always break up mercury oxid into its elements. Different substances have very different affinities.

18. Symbols of Elements. — An atom of copper is the smallest particle of copper that is found in any compound. The symbol of an atom of copper is Cu, that of an atom of oxygen is O, of one of sulfur is S. Every element has a symbol which stands for its atom. If more than one atom of an element is indicated a coefficient or a sub-exponent is used; 2Cl or Cl_2 means two atoms of chlorine, 7Hg indicates seven atoms of mercury.

A symbol is usually the first letter or letters of the Latin name of the element, which may or may not correspond to the English name. A few in which the Latin names differ from the English are: Sb (antimony) *stibium*, Cu (copper) *cuprum*, Pb (lead) *plumbum*, Fe (iron) *ferrum*, Hg (mercury) *hydrargyrum*, Ag (silver) *argentum*, Na (sodium) *natrium*, K (potassium) *kalium*, Sn (tin) *stannum*, Au (gold) *aurum*.

Exercises. — Give names to the following symbols: N, S, P, Si, B, Br, I, Na, K, Fe, Mn, Mg, Zn. Name these elements and the number of atoms in each: 3Bi , 5Sb , 7Ca , F_2 , I_2 , 6Br . Write symbols for 4 atoms of chromium, 7 of cadmium, 6 of barium, 2 of copper.

19. Symbols of Compounds. — A molecule of oxygen is represented by O_2 or 2O , one of hydrogen by H_2 or 2H .

Elements generally have two atoms to the molecule. The symbol (or formula) of the sodium chlorid molecule is NaCl , which shows that it is composed of one atom of sodium and one of chlorine. AgNO_3 is the symbol of a molecule made up of one atom of silver, one of nitrogen, and three atoms of oxygen. The formula of a compound has the symbols of the elements of which it is composed written one after the other and close together, as NaCl , KBr , HgS , NaNO_3 , CuSO_4 . In compounds a symbol always stands for one molecule — the smallest particle that exists — unless it has a coefficient. The latter shows the number of molecules; 3CaO means three molecules, each containing an atom of calcium and one of oxygen. CuCl_2 indicates that a molecule of the compound has one atom of copper united with two atoms of chlorine. An exponent applies only to the element which it follows. H_2SO_4 is a molecule of a compound which contains two atoms of hydrogen, one of sulfur, and four of oxygen. An exponent after a parenthesis multiplies all the elements within the parenthesis; $\text{Cd}(\text{NO}_3)_2$ is the same as CdN_2O_6 ; and $(\text{NH}_4)_2\text{SO}_4$ the same as $\text{N}_2\text{H}_8\text{SO}_4$.

Exercises. — The student must not think that every symbol which he can write represents a known and existing compound. The compounds whose molecular symbols are written by chemists have been analyzed and their composition is known. The beginner knows the symbols of these compounds only by memorizing them.

How many molecules are represented by the following? Also how many atoms of each element? 5KI , 6HgO , 3CuS , 2CaCl_2 , 4NaOH , AgNO_3 , $6\text{Cu}(\text{NO}_3)_2$, $3\text{Ca}_3(\text{PO}_4)_2$, $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_3\text{PO}_4$, $2\text{Fe}_2(\text{SO}_4)_3$, $3\text{Bi}_2\text{O}_3$, As_4O_6 , P_2O_5 .

20. Atomic Weights. — The atoms of any given element have a definite weight, peculiar to themselves, which is called the atomic weight. *The atomic weight of any*

element is the weight of its atom in terms of the weight of the hydrogen atom, which is the unit. Saying that the atomic weight of carbon is 12 means that its atom weighs 12 times the hydrogen atom. The atomic weight of oxygen is 16, hence the element is 16 times heavier than hydrogen, atom for atom. Every atomic symbol stands not only for an atom of the element, but for its atomic weight as well. Hydrogen is taken as the unit or standard of comparison, not because its atom weighs one grain or one gram, or any other simple number, but because it weighs less than the atom of any other element.

21. Molecular Weights. — *The weight of a molecule is found by adding the weights of all the atoms of which the molecule is composed.* The result is called the molecular weight of the substance, and is expressed in terms of the weight of a hydrogen atom. Thus symbols of elements and of compounds represent definite quantities, different for each substance. They are also sometimes loosely used for any indefinite amount, and in place of the name, as O may be used in place of oxygen, and H_2O of water.

Exercises. — By reference to the table, page 16, state what these symbols stand for, and how much by weight: Br, Na, As, N, Cu. Cooke named the weight of the hydrogen atom a *microcrith*, hence O weighs 16 microcriths, and 2O or O_2 32 microcriths. Compute the weight of these: 5H, 7Bi, 3Sb, 6Pb.

The molecules of many elements contain two atoms. How many molecules in these? 10N, 6I, 20Br, 3Cl, 7S. The molecule of an element is often written N_2 , O_2 , etc.

Find the molecular weight of $HgCl_2$. Proceed as follows:

$$\begin{array}{r} HgCl_2 \\ 199 + 2(35) \\ \hline 269 \end{array}$$

This means that the molecule weighs 269 microcriths, or the molecular weight is 269.

That of $(\text{NH}_4)_2\text{SO}_4$ is : $\frac{(\text{NH}_4)_2\text{SO}_4}{2(14 + 4) + 32 + 4(16)}$
132.

Find the molecular weights of NaCl , CuCl_2 , $\text{Pb}(\text{NO}_3)_2$, $\text{Ba}_3(\text{PO}_4)_2$.

Find the weights of these : 6HgO , $3\text{Fe}_2(\text{SO}_4)_3$, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. ($10\text{H}_2\text{O}$ represents water of crystallization, and belongs to Na_2CO_3 .) What fractional part of the molecule is water ?

TABLE OF ELEMENTS.

22. Following is a list of thirty-seven of the more common elements with their symbols and approximate atomic weights and usual valences. A complete list with accurate atomic weights may be found in the Appendix. For convenience the nearest integer only of these weights is given here. A () indicates an unusual valence.

NAME.	SYM.	AT. WT.	VALENCE.	NAME.	SYM.	AT. WT.	VALENCE.
Aluminum	Al	27	3	Iron	Fe	56	2, 3
Antimony	Sb	120	3, 5	Lead	Pb	205	2
Argon	A	20(?)	—	Magnesium	Mg	24	2
Arsenic	As	75	3, 5	Manganese	Mn	55	2, 4, 6
Barium	Ba	136	2	Mercury	Hg	199	1, 2
Bismuth	Bi	207	3, 5	Nickel	Ni	58	2
Boron	B	11	3	Nitrogen	N	14	3, 5
Bromin	Br	79	1 (5)	Oxygen	O	16	2
Cadmium	Cd	111	2	Phosphorus	P	31	3, 5
Calcium	Ca	40	2	Platinum	Pt	193	4
Carbon	C	12	4 (2)	Potassium	K	39	1
Chlorin	Cl	35	1 (5)	Silicon	Si	28	4
Chromium	Cr	52	(2), 3, 6	Silver	Ag	107	1
Cobalt	Co	58	2 (3)	Sodium	Na	23	1
Copper	Cu	63	2 (1)	Strontium	Sr	87	2
Fluorin	F	19	1 (5)	Sulfur	S	32	2
Gold	Au	196	3 (1)	Tin	Sn	118	2, 4
Hydrogen	H	1	1	Zinc	Zn	65	2
Iodin	I	126	1 (5)				

23. Binary Compounds.—Elements have a single name, compounds usually have two names only, no matter if they contain three or more elements. Compounds may

for convenience be divided into two classes, binaries and ternaries. A binary compound has but two elements, a ternary has three or more. Common salt is an example of a binary, the symbol of its molecule is NaCl , and its chemical name is sodium chlorid. Water, H_2O , is another, its chemical name being hydrogen oxid. In writing the symbol of a binary, the metallic or positive element is usually written first, followed by the non-metallic or negative element, as CuO , Fe_2O_3 . The same principle applies in representing ternaries. In naming a binary, the name of the first or metallic element is generally given entire, but the second name changes its ending — usually dropping the last syllable — and affixes the ending *id*. HCl is hydrogen chlorid, NaBr sodium bromid, CaS calcium sulfid.

Note that the pronunciation of *id* is as in *bid*, not as in *wide*. The naming of ternaries is given in Chap. XII, being too complex for the present.

Exercises. — An *oxid* is a compound of oxygen and some other element, as HgO , mercury oxid. Name several metallic oxids, without symbols. A *chlorid* is a compound of chlorin and some other element. Name half a dozen. What is a *bromid*, an *iodid*, a *sulfid*, a *carbid*, a *silicid*, a *phosphid*, a *fluorid*, a *hydrid*, a *nitrid*? Give illustrations of each. Affix the proper name to these symbols, writing them in a vertical column: HCl , CuCl_2 , SbCl_3 , NaBr , NaI , KBr , AgCl , AgI , HBr , HI , HgO , ZnO , ZnS , NiS , CaO , Ca_3P_2 , H_2S , H_3P , Na_3As , AuCl_3 .

Write symbols for four molecules of sodium bromid, one of silver iodid (always omit coefficient one), eight of potassium bromid, ten of hydrogen chlorid, seven of zinc oxid, three of zinc sulfid, and one each of hydrogen fluorid, potassium iodid, silver chlorid, magnesium oxid.

24. Prefixes. — In most of the above cases there is one atom only of each element in the molecule, as HgO . But some elements will not unite in that way. Antimony and chlorin do not form SbCl , but rather SbCl_3 ,

one atom of the metal requiring three atoms of the non-metal to form a molecule. There are five oxids of nitrogen known, the symbols of the molecules being N_2O , N_2O_2 (or NO), N_2O_3 , N_2O_4 (or NO_2), N_2O_5 . These are named as follows:

N_2O	nitrogen monoxid	(mono = one, first or lowest oxid).
N_2O_2 (or NO)	" dioxid	(di = two, or second).
N_2O_3	" trioxid	(tri = three, or third).
N_2O_4 (or NO_2)	" tetroxid	(tetra = four, or fourth).
N_2O_5	" pentoxid	(pente = five, or fifth).

Exercises. — If a given element has more than one oxid, chlorid, bromid, etc., the above prefixes are used. There are two oxids of phosphorus, P_2O_3 and P_2O_5 . Name each. Also name As_2O_3 and As_2O_5 , Sb_2O_3 and Sb_2O_5 . There are two oxids of carbon, CO and CO_2 . The former is carbon monoxid, the latter carbon dioxid. Name these: H_2O and H_2O_2 . FeS and FeS_2 are often called respectively *ferrous sulfid* and *ferric sulfid*. In the same way name Sb_2O_3 and Sb_2O_5 , $SbCl_3$ and $SbCl_5$, As_2O_3 and As_2O_5 , P_2O_3 and P_2O_5 .

25. Equations. — A chemical equation is a short algebraic expression of a chemical change. When we heated together the mixture of iron and sulfur and obtained iron sulfid, a reaction took place, which we may describe by saying that iron united with sulfur and formed iron sulfid, or iron + sulfur = iron sulfid. But a definite quantity of iron united with another exact quantity of sulfur and made still another definite quantity of the sulfid, viz., one atom of iron with one atom of sulfur formed a molecule of iron sulfid. Hence we may express the equation by symbols: $Fe + S = FeS$. On the large scale of the experiment millions of atoms of iron combined with an equal number of atoms of sulfur, and hence the equation with one atom of each is the briefest and most accurate way to represent what took place. We may further state that, as the atomic weight of iron is 56 and that of sulfur is 32, then 56 parts by weight of iron combined with 32 parts of sulfur to form 88 parts of iron sulfid by weight. $Fe + S = FeS$
 $56 + 32 = 88$.

In a similar way write out and explain the equation which represents the reaction on heating copper and sulfur. Every chemical experiment may be represented by one or more equations, if we know the result.

CHAPTER III.

OXYGEN.

26. The date of the discovery of oxygen, Aug. 1, 1774, has been called "the birthday of chemistry." The true explanation of oxygen in combustion gave us the first real knowledge of chemistry as a science, and overthrew the Phlogiston theory, which had been held for nearly a century. It is thus in its history as well as in its properties one of the most interesting of the elements. Though an invisible gas, we may learn by experiment how this first element of our study is separated from its compounds, and what are its properties and uses.

27. History. — Priestley, an English chemist, first prepared the element in 1774 by heating mercury oxid, HgO . Scheele, a Swedish apothecary, prepared it the next year, but independently, from mercury oxid, also from manganese dioxid, MnO_2 , and from potassium nitrate, KNO_3 , and named it "fire air." Lavoisier, a French chemist, first gave the true explanation of combustion, and in 1778 named the newly discovered substance oxygen, from an idea that it was the true *acid-former*, which the word means. This idea was afterwards modified.

28. Occurrence. — Oxygen is the most abundant of all the elements on the surface of the earth. It is found both combined and free. In the free or uncombined state it exists only in the atmosphere, of which it makes about one-fifth, being mixed but not combined with a much larger quantity of nitrogen, and a few other substances. It is found in almost all the great classes of compounds on the globe. Oxygen makes up eight-ninths of all water,

rocks are nearly half oxygen, and plants and animal bodies contain a very large percentage of it. In all these except air it exists combined with other elements in compounds either solid, liquid, or gaseous. Its existence in the sun is still a matter of question.

29. Preparation. — As it cannot be easily separated from the nitrogen of the air with which it is mixed, it is (for use in the laboratory or elsewhere) set free from some of its compounds. Among many of these compounds we may mention three classes which yield it quite readily, *viz.*, chlorates, nitrates, and oxids, from each of which it is separated by the application of heat. Priestley first prepared the element by the following experiment,

except that he used the sun's rays focused by a large lens instead of a lamp.

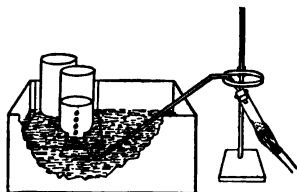


FIG. 7.

Exp. 10. — Put into an ignition tube 5 or 10^g of mercuric oxid, HgO , attach a delivery tube, and connect with a pneumatic trough, on the shelf of which is an inverted bottle or receiver filled with

water. Heat the tube, using a Bunsen flame, and after a minute collect the escaping gas in the receiver (Fig. 7). When it is filled remove the receiver, using the glass plate, and place it upright, covered (Fig. 8). Take out the delivery tube as soon as the lamp is removed, to prevent the water from being forced into the tube. Look on the sides of the tube for a deposit (called a sublimate), and describe it. The heat has dissociated or broken up the molecules of mercury oxid into the elements, mercury and oxygen. The former is first vaporized, then sublimed on the tube; the latter is collected over water. The equation to represent the reaction is $\text{HgO} = \text{Hg} + \text{O}$. Affix the molecular and atomic weights and then explain the equation, as in the case of FeS (page 18), this being a case of decomposition, not synthesis.

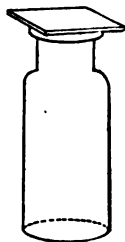


FIG. 8.

Exp. 11. — Draw aside the cover, and thrust a lighted splint into the receiver of oxygen. Note how vigorously it burns. Blow out the flame, and thrust the glowing end of the splint into the receiver. Oxygen unites with carbon to make carbon dioxide.

This preparation from mercuric oxid is a slow and expensive process. The element is readily liberated from potassium chlorate — chlorate of potash — KClO_3 , by the action of heat, and this is the usual means of obtaining it in the laboratory. At some 400° the compound breaks up into potassium chlorid and oxygen, but if mixed with half or more of its bulk of manganese dioxid — black oxid of manganese — MnO_2 , it breaks up at 200° , and the evolution of gas is more regular and less violent. The MnO_2 is probably not decomposed at this temperature, but remains unchanged at the end of the experiment.

Exp. 12. — Prepare apparatus as in Exp. 10, having several inverted receivers. To invert them grasp each as in Fig. 9. Mix on paper 5¢ of potassium chlorate, KClO_3 , and about the same amount of manganese dioxid, MnO_2 , put them into a test tube, attach the latter to the apparatus, heat the tube, and collect the gas. Remove the tube, receivers, etc., and save the gas for subsequent experiments.



FIG. 9.

The reason why MnO_2 lowers the decomposing point of the chlorate is not certain. By some it is thought that the MnO_2 is first reduced to a lower oxid, Mn_2O_3 , and then at once re-oxidized. Other oxids act in a similar way. The equation for the breaking up of chlorate of potassium is $\text{KClO}_3 = \text{KCl} + 3\text{O}$, which shows that each molecule of KClO_3 is broken up into a molecule of KCl , potassium chlorid, and 3 atoms of oxygen.

30. Other Methods. — Oxygen can be obtained from very many other compounds, as from water by electrolysis (Chap. IX), and from manganese dioxid at a white heat. At 550° barium protoxid, BaO , heated in the air, becomes barium dioxid, BaO_2 . At 800° BaO_2 again becomes BaO , giving up half its oxygen. To make the gas on a large scale and

cheaply, steam, H_2O , is forced over sodium manganate, Na_2MnO_4 , at low red heat.¹ $2\text{Na}_2\text{MnO}_4 + 2\text{H}_2\text{O} = 4\text{NaOH} + \text{Mn}_2\text{O}_3 + \widetilde{3\text{O}}$. The first two products, NaOH and Mn_2O_3 , can be changed back into Na_2MnO_4 by forcing air instead of steam over them, without change of apparatus, thus making the process continuous. $4\text{NaOH} + \text{Mn}_2\text{O}_3 + \widetilde{3\text{O}} = 2\text{Na}_2\text{MnO}_4 + 2\text{H}_2\text{O}$.

31. Properties. — *Physical.* Oxygen is a colorless gas without taste or odor, and is a little heavier than air. It is soluble in water, 25 vols. of water dissolving 1 vol. of O at 5° . — *Chemical.* Very active chemically, it unites with all elements except fluorin and bromin. A compound of oxygen with another element is known as an oxid. With some elements it combines much more readily than with others. Its affinity for hydrogen and carbon is great even at temperatures not much above the ordinary, while with nitrogen it will not combine except at the heat of the electric arc, though indirectly it forms five different compounds with that element (Chap. XXII). Oxygen dissolves rapidly in potassium pyrogallate.

The metals gold and platinum will form oxids only by indirect reaction, not by direct union. Ozone will oxidize silver directly. The tendency of oxygen to combine with almost everything is a reason for the oxidation, rust, and decay of so many substances. Its oxidizing power is assisted by the presence of water and many other compounds (as well as by micro-organisms), since pure dry oxygen is usually very slow in combining power at ordinary temperatures, and sometimes even is entirely inert. Water is only a chemical compound of hydrogen and oxygen; iron rust is a compound of iron, oxygen, and water. The burning of wood or coal gives rise to carbon dioxid, CO_2 , and water. Small fires and great conflagrations are due to this invisible gas uniting with other elements. Decay of animal and vegetable matter, though not due mainly to oxygen, is very much hastened by its presence. It is the union of the oxygen of the air with carbon and hydrogen in our blood and tissues that keeps up the heat of the body and supports life. Violent physical

¹ These equations may be omitted until the subject is reviewed.

exercise causes rapid oxidation, and we then breathe fast. Animal and vegetable life would cease to exist without oxygen (Chap. XXI). The great tendency of oxygen to unite with other elements—which tendency we call chemical affinity—may be shown by the following experiments.

Exp. 13.—Put a very small piece of sulfur into a combustion cup (Appendix), ignite it by directing the flame upon it, and then lower it into a receiver of oxygen (Fig. 10). Note the vigor and color of the flame, and very cautiously try the odor of the product, which is sulfur dioxide, SO_2 . Write the equation, remembering that the factors, which are always written on the left of the equation, are the substances used to make the experiment, *viz.*, oxygen and sulfur in this case, and the product is the result obtained, in this case sulfur dioxide. Affix the weights, and state in what proportion the elements unite.

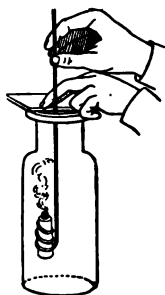


FIG. 10.

Exp. 14.—Balance a small piece of charcoal on the cup, set it on fire, and lower it into a receiver of oxygen. The equation in this case is $\text{C} + 2\text{O} = \text{CO}_2$. State the factors and product, affix the weights, and explain. Observe the residue. Is there any flame?



FIG. 11.

Exp. 15.—Put into the cup a small piece of phosphorus,—using forceps, not fingers, for this,—set it on fire by just touching it with a hot wire, and lower it into a receiver of oxygen. The fumes are phosphorus pentoxid, P_2O_5 . They soon settle, showing the product to be a solid. Write the equation.

Exp. 16.—Take in the forceps a piece of picture wire, tip the end with a bit of sulfur, set the latter on fire, and thrust it into a receiver of oxygen, partly filled with water or sand (Fig. 11). Iron burns with scintillations, giving iron tetroxid, Fe_3O_4 .

Exp. 17.—Set on fire a piece of magnesium ribbon held with forceps, and thrust it into a receiver of oxygen. The product is MgO .

32. Oxidation.—A slow combination is liable to take place at usual temperatures, but in order to burn in oxygen, most substances must have increased heat. Iron oxidizes or rusts in moist air, combining with oxygen to form an oxid of iron. *Oxidation in a restricted sense, as here used, is the process of combining oxygen with some other element to form an oxid. Combustion is oxidation attended with heat and light.*

Exp. 18.—Dip a bright piece of iron into water, remove, and leave it in your locker for a few days, then examine the surface.

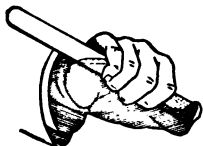


FIG. 12.

Exp. 19.—File a piece of lead until it is bright, and leave it for several days. The coating is an oxid of lead.

Exp. 20.—Pour about 5^{cc} of potassium pyrogallate solution into a test tube filled with oxygen, cover the tube with the thumb, and shake it well (Fig. 12). Open the tube under water. The liquid dissolves oxygen and becomes black.

33. Effects of Undiluted Oxygen.—If the atmosphere were undiluted oxygen it would be next to impossible to extinguish fires once started, and the entire surface of the earth would soon be stripped of life and burnt to a cinder. A rabbit was kept in the pure gas for three weeks. He ate voraciously all the time, but grew thin. It is claimed that man could live but a short time in the undiluted gas, that his motions would be very rapid, and that he would soon burn out his life as a candle or a stick burns out quickly in it. The nitrogen is supposed to dilute the air and to make it fit to be breathed. It is thought, on the other hand, that the haemoglobin of the blood can combine with only a definite quantity of oxygen, even if undiluted, and that the pure gas can be breathed with an effect not different from what air would have. The question is still an open one.

34. Liquid Oxygen. — Oxygen can be condensed to a liquid — and even a solid — by cold and pressure. Compressed oxygen stops fermentation and is a deadly poison.

35. Tests. — The combustion of sulfur, carbon, etc., in oxygen is the usual test applied to the element. Nitrogen monoxid, N_2O , also supports combustion. The solution of the element in a solution of potassium pyrogallate mentioned above is a valuable test and means of separation in analysis.

36. Uses. — The principal use of undiluted oxygen is in the production of the calcium light for stereopticon views and in theatres. Here it is burned with hydrogen, the flame being forced against a stick of lime. The effect is to give a brilliant white light. The use of oxygen in nature is to support combustion and to oxidize the animal system and support life.

CHAPTER IV.

NITROGEN.

37. Nitrogen is the chemical opposite of oxygen. The latter element has strong affinities, the former appears to have weak attraction for most elements. Oxygen is found almost everywhere, nitrogen exists only in the air and in comparatively few compounds. Oxygen illustrates chemical activity, nitrogen chemical inertia. Oxygen supports combustion, nitrogen does not. Oxygen sustains life, nitrogen has no physiological effect when inhaled, though it is a constituent of many animal tissues.

38. History. — This gas was first made known by Rutherford, an English botanist, in 1772. Lavoisier called it *azote* — a non-supporter of life. Rutherford found that when animals inhaled a confined portion of air there were formed two products which would not support life. One of these, carbon dioxid, CO_2 , he absorbed in sodium hydroxid solution, NaOH , and the other he found would not dissolve in it. Chaptal named the latter *nitrogen* from its existence in nitre, KNO_3 .

39. Occurrence. — It occurs free in the atmosphere — of which it makes not far from $\frac{1}{5}$ by volume, about 78%, — and in volcanic gases. There are several compounds, the three most abundant being nitrites, such as KNO_2 , potassium nitrite; nitrates, as NaNO_3 , sodium nitrate; and ammonium compounds, as NH_4Cl , ammonium chlorid. Besides these, organic matter, both vegetable and animal, contains nitrogenous compounds. The atmosphere is the ultimate source of all nitrogen in these compounds.

40. Preparation. — *From Air.* The usual mode of obtaining free nitrogen is to separate it from the other constituents of the air, especially oxygen. The latter may be burned out by phosphorus from a confined portion of the air (Fig. 14). $2P + 5O = P_2O_5$. The dense white fumes of phosphorus pentoxid, P_2O_5 , gradually subside and dissolve in the water, leaving the receiver about four-fifths filled with nitrogen. Water rises to fill the other fifth previously occupied by oxygen. Oxygen may also be burned out by passing a current of air over red-hot copper in a confined tube, heated in a furnace (Fig. 13). Copper oxid, CuO , is formed as a black solid and left behind in the tube, while nitrogen passes on and can be collected over water. $Cu + O = CuO$. In either case about 1% of the residual gas is argon. Liebig separated N by dissolving out the oxygen of the air in potassium pyrogallate solution.

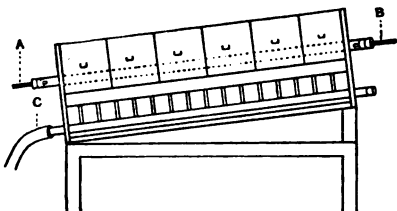


FIG. 13. — The furnace is heated by gas entering at C. Air is forced in at A, and nitrogen escapes at B.

41. From compounds the element may be liberated in several ways: (1) Passing chlorin into a strong solution of ammonium hydroxid, NH_4OH . $4NH_4OH + 3\widehat{Cl} = 3NH_4Cl + 4H_2O + \widehat{N}$. Great care must be exercised in this experiment, as a weak solution of the hydroxid is liable to form the very dangerously explosive nitrogen chlorid, NCl_3 . Towards the end of the experiment, also, when the ammonia is mostly combined, the same thing may occur. (2) Heating ammonium nitrite, NH_4NO_2 , liberates nitrogen. $NH_4NO_2 = 2H_2O + 2\widehat{N}$. (3) By heating ammonium dichromate, $(NH_4)_2Cr_2O_7$. $(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + 2\widehat{N}$.

Exp. 21. — Arrange a combustion cup as in Fig. 14, passing the wire down through the orifice of the shelf of a pneumatic trough, and fasten-

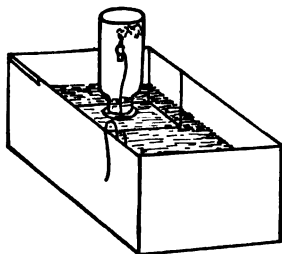


FIG. 14.

ing it on the side. Have the cup high enough to reach halfway up an inverted receiver, and the water to cover the shelf some 2^{cm}. With the forceps place in the cup a dry piece of phosphorus, — roll it lightly on paper, — touch it with a warm (but not too hot) wire, and cover the cup at once with the receiver (Fig. 14). Hold down the receiver tight at first, and see whether any air is forced out by the heat. Let the product settle and the gas clear.

O has combined with P and formed solid P_2O_5 , which settles and dissolves in the water. Water rises and takes the place of the O. The superincumbent gas is N. Remove the receiver, keep it upright and covered, with the water in the bottom, for Exp. 23.

Exp. 22. — Mix about 10% of ammonium chlorid, NH_4Cl , with 15% of sodium nitrite, $NaNO_2$, put the mixture into a small flask, attach a delivery tube, and connect with inverted bottles filled with water over a pneumatic trough

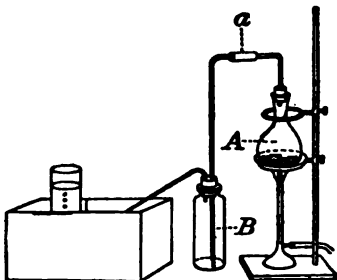


FIG. 15.

(Fig. 15). Apply heat gently till action begins, and then remove the lamp. The gas collected is N. $NH_4Cl + NaNO_2 = NaCl + 2H_2O + 2\widehat{N}$.

42. Properties. — *Physical.* Nitrogen when pure is a colorless gas having no taste or odor. It is very little lighter than air, and only slightly soluble (about 1%) in water. Like other gases it has been liquefied and solidified (Chap. XXVIII).

Chemical. It is very inert, not combining at ordinary temperatures with other elements. It neither burns nor

supports combustion. It is not poisonous, but gives no aid in supporting life. Four-fifths of each breath is nitrogen, which is inhaled and expelled without any physiological action. At a very high temperature it can be made to unite with some other elements, like oxygen and hydrogen. The electric spark passed through a tube containing air (or a mixture of O and N, Fig. 16) will gradually cause the two elements to combine and form an oxid of nitrogen. Electrical discharges during a thunderstorm also combine N and O

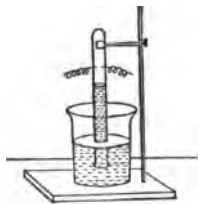


FIG. 16.

to form nitrogen trioxid, N_2O_3 , and tetroxid, NO_2 . These unite with water in the air to form nitric acid, HNO_3 , small quantities of which exist in the atmosphere. In parts of Europe it is estimated that 2 lbs. of the acid fall annually on an acre of ground. At times there is enough to make rain water sour. The very inertness of this element makes its compounds of great value in explosives, almost all of which contain some compound of it. Familiar examples are gunpowder, nitro-glycerin, and dynamite. A high temperature, a spark, or a blow will suddenly break up the solid compound, freeing nitrogen and other gases, producing an effect called *an explosion*, as the gases formed occupy hundreds of times the volume of the solids, and must have "standing room."

There are a few elements for which nitrogen has affinity. Boron is one which when heated unites with it with great vigor, boron nitrid, BN , being the product. Another one is magnesium. This must first be heated red hot in a tube, and a current of nitrogen then passed over it. The product is Mg_3N_2 . Lithium also unites with it. Minute vegetable life — micro-organisms of certain sorts — have lately been found efficacious in

transforming the nitrogen of the air directly into compounds, such as ammonia, nitrites, and nitrates.

43. Tests. — The tests of nitrogen are almost all negative. Several other gases will not support combustion, nor burn. Carbon dioxid, CO_2 , and nitrogen dioxid, NO , are examples; but these have definite positive tests, entirely different from nitrogen, whose chemical inertia is its important characteristic.

Exp. 23. — Thrust a lighted splint into the receiver of N (Exp. 21). See whether it supports combustion, or burns, or neither. Try a bit of burning sulfur or phosphorus. Drop a piece of blue litmus paper into the liquid. Save the latter for Exp. 24.

Exp. 24. — Pour into a graduate the liquid from Exp. 23, and note the number of centimeters. Then fill the whole receiver with water and measure it. Find the per cent of oxygen in air by comparing the two numbers, remembering that the first stands for the volume of oxygen in the volume of air represented by the second. It should be not far from 20%. If much air was forced out at the beginning of Exp. 21, there would be too large a per cent of oxygen.

Exp. 25. — Measure the capacity of a small test tube (use a graduate or, better, a burette), and put in a measured quantity, say 5^{cc}, of a solution of pyrogallol — pyrogallic acid, $\text{C}_6\text{H}_3(\text{OH})_3$ — in a little potassium hydrate solution. Cover the mouth of the tube with the thumb and shake it vigorously. Open it under water. If the water rises, have the level inside and outside the tube the same, then cover its mouth with the thumb and remove from the water. Measure the liquid now in the tube (or fill the tube with water and ascertain the number of centimeters it takes), then measure the capacity of the tube. Compute the per cent of oxygen and of nitrogen in air, as in Exp. 24.

44. Uses. — The action of nitrogen in the air is to dilute the active oxygen and prevent its too rapid action in combustion and respiration. The air is the great storehouse of the element from which nature draws for the preparation of those compounds useful for plants and animals, and valuable for commercial purposes.

CHAPTER V.

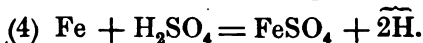
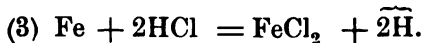
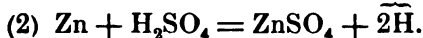
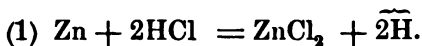
HYDROGEN.

45. — Hydrogen gas is the lightest of all known substances, its weight being $14\frac{1}{2}$ times less than air. Eleven liters of it weigh less than a gram. The hydrogen atom is the smallest particle of matter recognized in science. Lavoisier thought oxygen was the acid-former when he named that element, but hydrogen has since been found the essential element of acids.

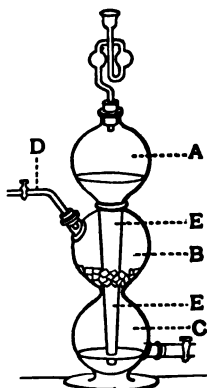
46. History. — The English chemist Cavendish in 1766 was the first to isolate and experiment with the gas, though Paracelsus, about 1540, obtained it by acting on metals with sulfuric acid, the result of which he described as “the rising of the wind.” Cavendish called the gas “inflammable air.” Lavoisier named it *hydrogen*, i.e., *water-former*.

47. Occurrence. — This element is rarely found in any quantity uncombined. It has been detected in volcanic gases and as a constituent of “natural gas”; also in coal mines in small amounts. It is given off in the decay of animal and vegetable matters. It is found in some meteorites, and in the atmosphere of the sun and fixed stars. In compounds it is very abundant and widely distributed. Of the gases composing water, hydrogen is one-ninth by weight, and two-thirds by volume. It is a necessary constituent of all acids and bases, and of plant and animal tissues.

48. Preparation. — Hydrogen is commonly prepared from acids, either hydrochloric, HCl , or sulfuric, H_2SO_4 , by the action of some metal, as zinc or iron. The acid should be diluted to dissolve the product, which is left in the generator. If H_2SO_4 is used it is necessary to dilute it, or SO_2 will form instead of H . The zinc, by virtue of its great affinity for chlorine (under the given conditions), drives out the hydrogen from its union with chlorine, and combines with the latter.



Kipp's Apparatus (Fig. 17) is a very convenient device



where considerable gas is wanted. Hydrogen can be obtained from water, H_2O , by action of certain metals, or by electrolysis. Sodium acts on cold water very vigorously and liberates half of the hydrogen, forming NaOH , sodium hydroxid, which dissolves in the water (Fig. 20). Potassium reacts similarly.

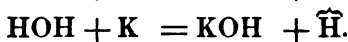
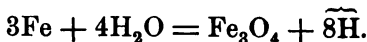


FIG. 17. — For description, see Appendix.

These metals thrown on water float around, and so much heat is liberated by the action of potassium on H_2O that both the gas and

the metal are set on fire. The same result occurs with hot water and sodium. Other metals, *e.g.*, iron, will decompose water at a high temperature. Bits of iron are put into a combustion tube which is heated to redness, and a current of steam is passed through the tube (Fig. 18).



49. Other Methods.—Water may be deprived of its oxygen by passing steam over hot carbon (Fig. 18), and hydrogen be thus liberated. At a red heat CO_2 is formed, at a white heat CO . These reactions take place in the formation of water gas (Chap. XXI), the H and the other gas being of course mingled.

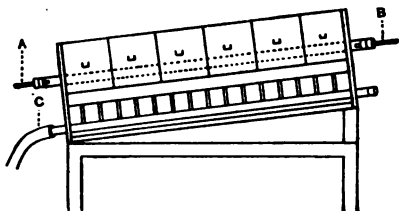
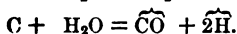
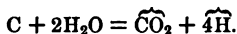
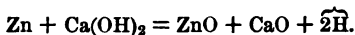


FIG. 18. — The furnace is heated by gas, entering at C. Steam is forced in at A, and hydrogen escapes at B. C or Fe is placed in the tube.



Zinc dust heated with slaked lime, $\text{Ca}(\text{OH})_2$, liberates H.



For electrolysis, see Chap. IX.

Exp. 26.—(Read the caution in Exp. 36.) Put 10 or 15g of granulated zinc into a hydrogen generator (Fig. 19), connect it with a trough and receivers, pour in water enough to cover the end of the thistle tube, and add little by little hydrochloric acid, collecting the escaping gas.

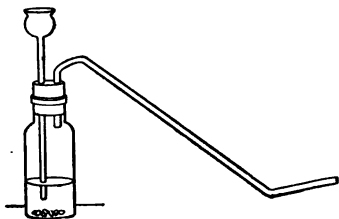


FIG. 19.

Exp. 27.—Cover with water a few pieces of zinc in an open test tube and add a little dilute sulfuric acid, enough for strong effervescence. Try to ignite the escaping gas.

Exp. 28. — Do this experiment like the previous one, substituting iron filings for the zinc.



FIG. 20.

Exp. 29. — Substitute hydrochloric acid for sulfuric in the last experiment, still using iron filings.

Exp. 30. — Drop a small piece of sodium into a receiver containing a little water, and cover the receiver with paper or cardboard (Fig. 20). As soon as action stops, try to ignite the gas in the receiver.

Exp. 31. — Place a piece of sodium in a wire spoon (Fig. 21), and bring an inverted tube of water over it, first putting the spoon under water.



FIG. 21.

50. Properties. — *Physical.* This is the lightest of gases, being 16 times lighter than oxygen. It can be poured upward (Fig. 24) and collected by upward displacement. When pure, it is colorless, and without taste or odor; but the impure gas made in the laboratory has both color and odor, and is poisonous. Hydrogen is but little soluble in water. Owing to its small vapor density it diffuses very rapidly (Chap. XXVIII). Being the lightest of gases its atom is taken as the unit of atomic weight, atomic volume, vapor density, etc. It has been reduced to a colorless liquid at -240° and under a pressure of 600 atmospheres, and, it is claimed, has lately been solidified.

Chemical. There are many elements, as carbon and phosphorus, with which hydrogen will not combine under ordinary conditions, though compounds of each with hydrogen are obtained indirectly. Hydrogen combines with boiling sulfur. It will not unite with most metals. In this respect it differs from oxygen. For a few elements it has great attraction. It burns readily, combining with

oxygen to form water, and has very strong affinity for chlorine — the two gases uniting in direct sunlight with explosive violence, and in diffused light slowly, making in each case hydrochloric acid, HCl . In darkness the mixture remains uncombined, each element retaining its original properties.

It has also affinity for Br and I, forming HBr and HI . Indirectly it forms compounds with S, P, As, etc., as H_2S , hydrogen sulfid, H_3P , hydrogen phosphid, H_3As , hydrogen arsenid. Its compounds with C are hundreds in number and are known as hydrocarbons, as CH_4 , C_2H_2 . H burns in O or in the air, because of the affinity of the two elements for each other at a high temperature. It burns with a blue, almost colorless, flame. It is called a *combustible*, and is a supporter of oxygen or chlorine combustion, but not of carbon, etc. A mixture of O and H explodes with dangerous violence when a flame is brought near it. At the moment of combination a great expansion takes place followed by contraction, as the liquid water occupies less than $\frac{1}{2000}$ of the volume of the original gases.

51. Oxy-Hydrogen Flame. — Hydrogen and oxygen in burning give the hottest flame known. The heat of the oxy-hydrogen blowpipe is not so intense as that produced by the electric arc, but is about 2000° . Clay is fused by it, and quartz is melted, and can be drawn into threads. Platinum fuses at the intense heat. The oxy-hydrogen blowpipe consists of two concentric tubes, the inner one carrying oxygen, the outer hydrogen (Fig. 22). At the end these two gases come together and are burned. The



FIG. 22. — A, hydrogen; B, oxygen; C, mixture and combustion.

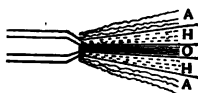


FIG. 23. — A, air; H, hydrogen; O, oxygen.

section (Fig. 23) shows the relations of the gases air, hydrogen, and oxygen at the exit of the tube. These become intimately mixed, thus furnishing the best conditions for combustion, and there should be twice as much hydrogen as oxygen by volume. The *calcium light* (also called lime or Drummond light) is made by putting into the almost colorless oxy-hydrogen flame a stick

of prepared quicklime. It then gives a dazzling white light, which has been seen for over one hundred miles. It is much used for stage effects

in theatres, and for stereopticon views. In place of hydrogen, illuminating gas is now employed.

52. Other Properties. — Hydrogen is not poisonous, but it does



FIG. 24.

not support life, and when inhaled it gives the voice a high, shrill sound. The lightness of hydrogen can be shown by counterpoising a large inverted beaker on one beam of a balance with weights on the other, and then pouring the gas upward into the inverted beaker, which then rises (Fig. 24). The rapid diffusion of hydrogen (Chap. XXVIII) is shown by plugging one end of a long tube with some porous material like plaster of

Paris, filling the tube with hydrogen, and inverting it over a receiver of water which may be colored. The water will rise in the tube (Fig. 25), as hydrogen escapes through the plaster faster than air enters.

Exp. 32. — Lift a receiver of hydrogen from the water, and thrust a burning splint into it (Fig. 26), while still inverted.

Exp. 33. — Half fill a receiver with water, and invert it in the trough, leaving the upper half filled with air. Fill the lower half with hydrogen from a generator, then bring the receiver, inverted, to a flame.

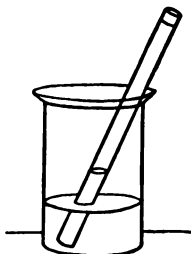


FIG. 25.

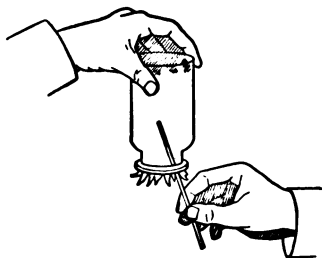


FIG. 26.

Exp. 34. — Try to pour a receiver of H up into one filled only with air, and let the air pass into the other (Fig. 27). In an instant bring each successively to a flame.

Exp. 35. — Collect H by upward displacement, using the apparatus in Fig. 28; then test the gas.

Exp. 36. — Draw out a piece of tubing to a small bore and break it. Attach this to a hydrogen generator, making a philosopher's lamp, and interposing a drying tube of calcium chlorid. When the gas begins to escape, test it by collecting a test tube full by upward displacement, and bringing it to a flame. If a sharp sound occurs, wait and soon test again, as air is mixed with hydrogen, and an attempt to light the gas would result in a dangerous explosion. If a slight muffled sound occurs, light the gas. Avoid pointing the tube towards any one. Lower several

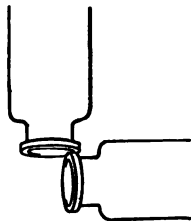


FIG. 27.

long glass tubes of different sizes over the flame (Fig. 29). Note any moisture and any sound. A musical note is often heard, but this is not peculiar to hydrogen, and is due to the vibration of the column of gas.

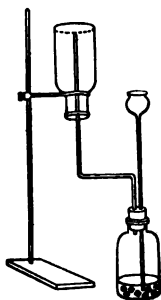


FIG. 28.

53. Occlusion. — It is found that hydrogen has the property of passing through certain metals with ease when they are red hot. Palladium, platinum, and even iron have this effect (but on no other gas than hydrogen), and it is supposed that the gas forms a compound (or an alloy) with the metal. The name given to this property is *occlusion*. It is not peculiar to hydrogen, but other gases have it. Oxygen is

occluded (or hidden away) by molten silver, but when the latter cools the occluded gas is thrown out in bubbles.

54. Tests. — The union of hydrogen with oxygen, to form water, and its union with chlorin and bromin serve as tests.

55. Uses. — The uses to which hydrogen was formerly put are now subserved mainly by illuminating gas. Two instances in point are its use in balloons and in the calcium light. Illuminating gas contains a large proportion of hydrogen, and the other main constituents

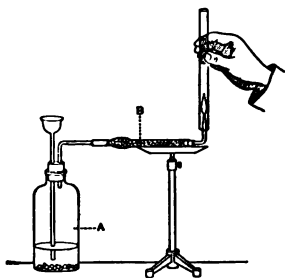


FIG. 29. — Philosopher's lamp. *A*, gas generator; *B*, drying tube of CaCl_2 . See Appendix.

are both light and inflammable. Besides, the gas is very much cheaper than hydrogen. Nothing, however, equals the latter for the pure oxy-hydrogen flame. Some of it is also used in chemical experiments, as a reducing agent, etc. Combined with other elements it is a necessary constituent of all living organisms. Other uses of its compounds are too numerous to mention here.

COMPARISON OF OXYGEN, NITROGEN, HYDROGEN.

	OCCURRENCE.		PREPARATION.	PROPERTIES.	USES
	UNCOMBINED.	COMBINED.			
O	Air.	Oxids, chlorates, nitrates, etc.	Heating oxids, chlorates, nitrates, etc.	Very active gas, supporter of combustion.	Combustion, breathing, oxy-hydrogen lamp, calcium light, oxidizing agent, etc.
N	Air.	Ammonium compounds, nitrites, nitrates, etc.	Burning O out of air by P or Cu. From NH_4OH and Cl.	Very inert gas, non-combustible, non-supporter.	Diluent in air, explosives, plant food.
H	Coal mines, oil wells, natural gas, volcanoes.	Water, acids, bases.	From HCl or H_2SO_4 and metal, decomposing H_2O , etc.	Very light gas, combustible, non-supporter.	Balloons, calcium light, in acids, bases, water, living organisms.

CHAPTER VI.

UNION BY WEIGHT.

56. In large chemical industries it is almost as necessary to know the right proportion for mixing substances as to know what to put together. If too much of any substance is used there will either be a waste of material, or a different reaction from the one desired will take place. Nature does not work at random. She follows laws which are always operative under the same conditions. Vary the conditions of an experiment and new laws are liable to intervene and change the result. *The essence of law is uniformity of action under like conditions.*

Every chemical experiment illustrates two laws: 1. *The law of Conservation of Matter.* 2. *The law of Definite Weight.* These may be called the fundamental laws of chemistry. A third, the *law of Definite Volume*, is often included, but as this is restricted to gases, it is not of universal application.

57. History.—The indestructibility of matter, and the fact that it cannot be created, seem to have been first clearly shown by Lavoisier in 1770. He weighed the substances used and the products obtained and found them equal. He was the first quantitative chemist. The law of definite or constant proportion by weight was firmly established as the result of a long controversy from 1799 to 1806 between Berthollet, who opposed it, and Proust, who favored it. Richter, 1792, announced it, and, later, Lavoisier.

58. Law of Conservation of Matter. — *The weight of the sum of all the products in an experiment is exactly equal to the weight of the sum of all the factors.*

According to this law there can be no loss of matter in any experiment, nor any matter created. New substances are formed, elements are separated from compounds, compounds are made from elements, solids are changed to liquids or invisible gases, and gases to liquids and solids, but there is no loss. Matter cannot be destroyed or annihilated, neither can it be created. It can only be changed or transformed, and the products must always weigh the same as the factors, though the volumes they occupy may be different. Hence in writing an equation, there must always be as many atoms of each element in the products as in the factors. Fewer atoms in the products than in the factors would mean a destruction of matter, more in the products would mean a creation of matter. In the equation

for preparing oxygen there are on each side one atom of K, one of Cl, and three of O. In every equation an equality should be traced. $\text{KClO}_3 = \text{KCl} + \hat{3}\text{O}$.



FIG. 30.

Exp. 37. — Put a small stopper upright on the bottom of a wide-mouth bottle, and on it place a dry piece of phosphorus (Fig. 30). Cork the bottle perfectly tight, and weigh the whole accurately. Set the bottle in direct sunlight, so that the phosphorus will take fire spontaneously. After combustion ceases weigh the bottle and its contents again, and compare with the previous weighing. Uncork the bottle, and then weigh again.

59. Law of Definite Weight. — *Any given chemical compound always contains the same elements, in the same ratio by weight.*

Potassium chlorate always contains potassium, chlorine, and oxygen, and always the same proportion of these elements by weight, *viz.*, 39 of K, 35 of Cl, and 48 of O. There is no variation from a fixed quantity in any true chemical compound. To mix chemicals in the right proportion for a given result, we must know the reaction which will take place, and must compute the molecular weights in that reaction; then we must mix quantities proportionate to the weights of the factors.

Exp. 38. — [This experiment to illustrate the above law would better be left for review, when the pupil will be more familiar with manipulation and composition.] Weigh accurately 4g of sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, crystals that have not effloresced, put it into a small beaker, previously weighed, and add little by little dilute HCl, covering the beaker loosely (Fig. 31). When the salt has all dissolved, evaporate the water, and then weigh the dry salt that is left with the beaker. Subtract the weight of the beaker, and the remainder is the weight of sodium chlorid, NaCl, obtainable from 4g of the carbonate. Do the experiment again, using a different weight of the carbonate, say 6 or 8g, and weigh the product obtained. See whether the two results vary for the amount of NaCl obtained from the weight of one gram of the carbonate. Except for inaccuracies in the experiment they should be the same.

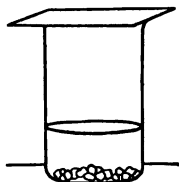
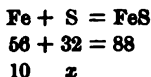


FIG. 31.

60. Application of the Laws. — Suppose we wish to prepare some ferrous sulfid, FeS, from its elements, in what proportion should we mix the latter? The equation which stands for the reaction must first be written: $\text{Fe} + \text{S} = \text{FeS}$. Next the atomic and molecular weights must be affixed: $\text{Fe} + \text{S} = \text{FeS}$ } This means that when iron and sulfur unite to form ferrous sulfid 56 parts by weight of iron always unite with 32 of sulfur to form 88 parts of the sulfid. We should then mix the elements in the proportion of 56g of iron to 32g of sulfur, or 7 to 4. Suppose we have 10g of iron, how much sulfur will combine with it? Arrange the work as follows, placing x under the required or unknown

$$\begin{array}{rcl} \text{Fe} + \text{S} & = & \text{FeS} \\ 56 + 32 & = & 88 \end{array}$$

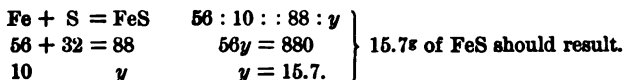
substance (S in this case), and 10 under the known or given substance (Fe in this case).



Evidently there is the same ratio between 56 of Fe and 32 of S as between 10 of Fe and x of S. This gives the following proportion: $56 : 32 :: 10 : x$, solving which we have $56x = 320$, $x = 5.7$.

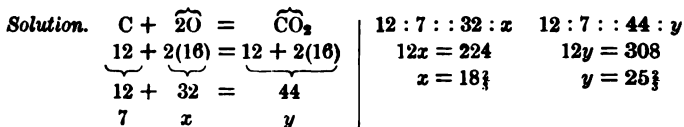
Thus 5.7% of sulfur are needed to combine with 10% of iron.

How much ferrous sulfid will be made? Arrange and solve as follows:



The proportion may be stated as follows: a given : a required :: b given : b required.

How much oxygen will combine with a piece of charcoal weighing 7%, and how much CO_2 will form?



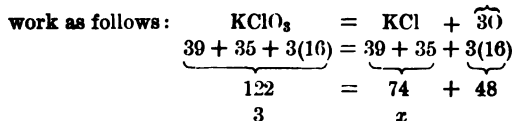
Hence $18\frac{2}{3}\%$ of oxygen are required and $25\frac{1}{3}\%$ of carbon dioxid are formed.

Exercises. — 1. How many grams of sulfur are needed to combine with 50% of copper to form copper sulfid, CuS , and how much CuS will it make?

2. How much SO_2 should form from burning 1 oz. of sulfur?

3. I wish to make 10% of P_2O_5 . How much phosphorus will it take?

4. From 3% of KClO_3 how much KCl ought I to obtain? Arrange the



Here KClO_3 , being the factor, must be put first. Solve the question.

5. Lead nitrate breaks up as follows: $\text{Pb}(\text{NO}_3)_2 = \text{PbO} + 2\widehat{\text{NO}_2} + \widehat{\text{O}}$. From 11% of it how much PbO should form?

6. What is the per cent of iron in Fe_3O_4 ? Arrange as follows and solve:

$$\begin{array}{rcl} \text{Fe}_3\text{O}_4 & = & 3\text{Fe} + \widetilde{4\text{O}} \\ \underbrace{3(56) + 4(16)} & = & \underbrace{3(56)} + \underbrace{4(16)} \\ 232 & = & 168 + 64 \\ 100 & & x \end{array}$$

Exercises.¹—1. Find the per cent of Fe in Fe_2O_3 . 2. In FeCO_3 . 3. In FeS_2 .

4. What is the percentage composition of H_2O ? 5. H_2S ? Per cents are always reckoned by weight (not by volume) unless otherwise specified. By percentage composition is meant the per cent of each element in the compound.

6. Find the percentage composition of alcohol, $\text{C}_2\text{H}_6\text{O}$.

7. What weight of O is needed to burn a diamond of $1\frac{1}{8}$ weight?

8. How much Cu will throw down 5 oz. of Ag from a solution of AgNO_3 ?

9. How much $\text{Pb}(\text{NO}_3)_2$ is required to make 10 lb. PbSO_4 ?

10. How much H_2SO_4 is required to make 10 lb. PbSO_4 ?

11. How much HNO_3 is required to dissolve 2 kilos of lead?

12. How much $\text{Pb}(\text{NO}_3)_2$ can be made from 2 kilos of lead?

13. How much Pb is needed to form 2 kilos of lead nitrate?

14. How much NaOH will neutralize (or react with) 50 lb. H_2SO_4 ?

15. How much H_2SO_4 will neutralize (or react with) 50 lb. NaOH?

16. A skeleton weighs 20 lb. and is 57% $\text{Ca}_3(\text{PO}_4)_2$. How many matches can be tipped with the phosphorus it contains, if one pound of the element tips a million matches?

17. How much silver nitrate can be made from 3 oz. of silver coin which is $\frac{9}{10}$ pure?

18. At 70 cents per ounce what is the value of the silver in $\frac{1}{4}$ lb. of silver nitrate?

¹ Some of these problems may be omitted till the book is reviewed, when the pupil will be more familiar with the reactions.

CHAPTER VII.

CARBON.

61. The forms of carbon differ so much from each other that we seem to be studying three different elements rather than one. This can be seen by examining side by side specimens of diamond, graphite, and charcoal. They do not appear at all alike. The diamond is very hard and lustrous; graphite is very soft, black, and greasy; and charcoal is black, porous, and easy to ignite. But there is one property which is the same for each, and proves that the three specimens are really the same element.

62. Allotropy of Carbon. — Allotropy — a name proposed by Berzelius, 1841 — means that an element exists in different forms, called allotropic forms, with varying properties. Many elements besides carbon are allotropic, as oxygen and sulfur. There are three allotropic forms of carbon: (1) Diamond, (2) Graphite, (3) Amorphous Carbon. The first two are crystalline; amorphous means not crystalline. These are all varieties of the same element, but most of the properties of one form differ from those of the others.

63. History. — Lavoisier in 1772 burned the diamond, and thus first distinguished it from quartz. Tennant and also Mackenzie about 1796 obtained the same weight of CO_2 from equal weights of diamond, of graphite, and of charcoal. Graphite was known to the alchemists, and pencils were made from it in 1565. Charcoal was thought by the phlogistonists to be very pure phlogiston.

DIAMOND.

64. The diamond is found in only a few places on the earth, as southern Africa, Brazil, Borneo, and is not abundant. The largest one ever found weighs $971\frac{1}{2}$ carats (less than half a pound), and is valued at half a million dollars. Carbonado—a black variety of diamond harder even than the gem, and used for drilling rocks—has been found which weighs 2 pounds. Diamond is

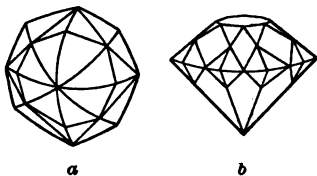


FIG. 32.—Diamond. *a*, uncut; *b*, cut.

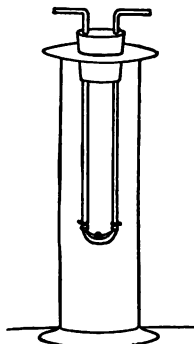


FIG. 33.

the hardest substance known, with the possible exception of the artificial product boron. Its value as a gem is due to its scarcity, lustre, hardness, and unchangeability. It is also used to cut glass, and its powder to grind other diamonds. Moissan has obtained minute crystals supposed to be diamonds by fusing Fe and C. The crystals were found in the molten metal. At 1200° there appeared a mixture of amorphous carbon and graphite, at 3000° only graphite, at 3000° under great pressure, diamond. Diamond can be burned by fastening it with platinum in a jar of oxygen between the two terminals of a battery, and passing over it a strong electric current (Fig. 33).

GRAPHITE.

65. Occurrence.—Graphite—also called plumbago, black lead, etc.—is quite abundant and widely diffused in the oldest rocks of the earth, in Ceylon, Siberia, Canada, California, New York, and elsewhere. In some places it occurs as a continuation of beds of anthracite coal, and thus indicates an origin like the latter. As coal

comes from preëxisting plant life, graphite would seem to come from the same.

66. Formation.—This form of the element can be prepared only in small quantity, and under exceptional conditions. In the iron furnace, small scales of graphite are separated from the solidifying iron, whereas the carbon originally put in was amorphous.

67. Properties.—It is a very soft, black, unctuous, crystalline mineral. It can scarcely be fused, and like other forms of carbon has no known solvent at ordinary temperatures. It is a good lubricant, takes a fine polish, and leaves a black mark on paper. It can be burned only at the highest temperature, when it forms carbon dioxid, CO_2 . A given weight of pure carbon, either in diamond, graphite, or charcoal, will combine with oxygen to form a fixed weight of carbon dioxid.

68. Uses.—Plumbago has a large number of uses, such as for lubricants, linings for crucibles in which iron, steel, etc., are melted, for foundry facings (to make smooth castings), electrotpe facings, lead pencils, stove polish, and polish for gunpowder.

AMORPHOUS CARBON.

69. Varieties.—There are many sorts of amorphous carbon. The most common are *charcoal*, *lamp-black*, *bone-black*, *coke*, *gas carbon*, and *mineral coal*. Mineral coal is a natural product, but the others are mainly artificial. Wood, oil, illuminating gas, and all animal or vegetable tissues and most of their products are compounds of carbon. Limestone, CaCO_3 , is another very common compound of carbon.

70. Charcoal is made by heating wood for a time out of contact with air. The compounds forming woody fiber or cellulose are broken up by heat, and volatile gases are driven off. The process is called *destructive distillation*, because the original compounds are destroyed. What is left is *carbon* with a very

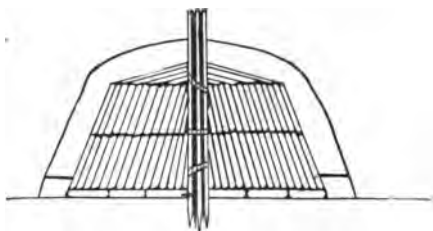


FIG. 34. — Wood arranged for making charcoal, and covered with turf.

little mineral material which the vegetable matter absorbed while growing, and which on burning the coal is left as ash. The gases formed in the experiment are water vapor, compounds of hydrogen and carbon (which are called hydrocarbons, and are combustible), carbon dioxid, etc. Acetic acid and tar are also formed. The coal is not over two-thirds the volume of the original wood, or one-fourth its weight. On the large scale it is made by piling wood in a conical heap (Fig. 34), covering it with sods, leaving small openings for air, so as to burn only a little of the wood, then setting fire to it and letting it smoulder. Charcoal has a great variety of uses, as for heating, reducing ores, etc.

71. Lamp-black is, next to gas carbon, the purest form of amorphous carbon. It is formed by igniting turpentine, naphtha, and various oils which are mostly hydrocarbons, and collecting the unburned carbon or smoke (Fig. 35). Not enough air must be admitted for complete combustion. Lamp-black is the basis of printers' ink, India ink, black paint, etc. "Natural gas" gives a good

variety of it. Hydrocarbons may be solid, liquid, or gaseous. Those rich in carbon are often solid, and those rich in hydrogen are often, but not always, gaseous.

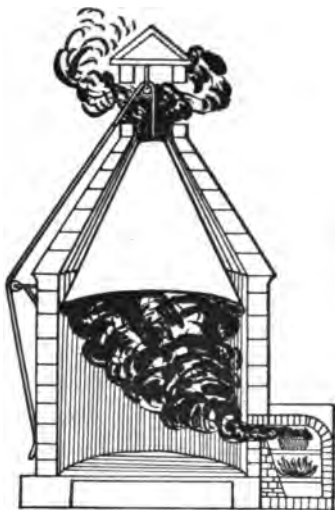


FIG. 36.

72. Bone-black (or animal charcoal) is obtained by the destructive distillation of bones. The volatile portions, consisting of water, ammonia, etc., are driven off, and carbon, together with a large amount of calcium phosphate, is left. Bone-black is used to refine sugar.

73. Coke.—This is the residue left after distilling soft coal. The distillation is like that of wood, the volatile gas is used for illumination, and the coke is carbon with some ash. Coke burns without flame and is utilized in the iron reduction furnace, and to some extent for heating. Like charcoal, it is very porous, but requires a high temperature to set it on fire.

74. Gas Carbon is formed in the preparation of coke, as well as of illuminating gas, and is named from the latter. It is very dense and hard, extremely difficult to burn, and has little use.

Exp. 39.—Put into a small Hessian crucible a few pieces of wood (say $\frac{1}{2}'' \times \frac{1}{4}'' \times \frac{1}{4}''$), and cover them with sand. Arranging the apparatus as in Fig. 36, apply heat for half an hour, noting any gases, their

odor, combustibility, etc., and any effect on the sand. Remove the pieces of wood (now charcoal), and examine as to color, lustre, weight, volume, porosity, brittleness, combustibility, etc. This experiment may be done with sawdust in an ignition tube.

Exp. 40.—Light a candle, and hold a short glass tube, a crayon, or an evaporating dish in the flame for a moment. Do the same with the flame of a kerosene lamp. Try it with a Bunsen lamp flame, first closing the lower orifices of the lamp. Do solid particles of carbon come through the gas pipes with the gas? Explain.



FIG. 36.

MINERAL COAL.

75. Occurrence.—This product is found in almost every country on the earth. The United States has far the largest amount. More than 300,000,000 tons are mined every year, and it is estimated that there is enough in the crust of the earth to make a layer 3 feet thick over the land surface.

Formation. Mineral coal was originally wood and other vegetable matter. It might be called fossilized vegetation. For millions of years the earth has contained life



FIG. 37.—Contorted strata in earth's crust. The black strata shows coal formation.

as it does to-day. During all the ages the earth's crust has been subject to gradual and slow upheaval and subsi-

dence, making contortions in the strata that were originally horizontal (Fig. 37). In favored localities plant life has been buried, and age after age has covered it with additional deposits of earthy material until (it may be at the

depth of thousands of feet) it has been subjected to a slow distillation by the heat from the earth's interior. Millions of years may be consumed in changing wood to mineral coal by this action of heat, pressure, and percolating waters. The action is called metamorphism. It is a destructive distillation of vegetation on an immense scale for an unlimited time. If the distillation is complete, graphite seems to be the product, for that contains about 100% of carbon. If less complete, hard coal, called anthracite (which may have 90% carbon), results. If still less perfect, soft or bituminous coal having some 60% carbon is formed. Peat has about 40% carbon.

76. Varieties.—Commonly reckoned there are two varieties of mineral coal: (1) Anthracite, (2) Bituminous. The first is hard coal, the second soft. Bituminous has several sub-varieties, as *Cannel*, *Lignite*, *Brown coal*. These are all less pure forms of carbon than true bituminous coal. *Peat* is the stage next lower than brown coal, and the carbon in it is unconsolidated. *Turf* is a still less pure form of carbonaceous material, made up of roots of plants.

77. Anthracite.—This is the richest in carbon, some varieties having 90 to 95 per cent. It has lost most of its gases by natural distillation, burns with but little flame, and requires a high temperature to set it on fire. It is very much used for heating houses, especially in New England, but is more expensive and far less abundant than soft coal.

78. Bituminous coal blackens the hands, burns with much flame, and at a lower temperature than hard coal, gives off volumes of smoke, and is richer in hydrocarbons, but less rich in carbon, than anthracite. As it gives up so many gases, it is the coal which furnishes illuminating gas and is made into coke. *Cannel* is a variety of bituminous, so rich in hydrocarbon gases that it can be ignited by a match or candle (whence, it is said, the name). This is a very expensive variety, found in but few localities, and used in fireplaces.

79. Properties of Charcoal.—Charcoal is a black, amorphous, porous substance, without taste or odor. It

is practically insoluble in any liquid, and cannot be melted or vaporized (except in the electric furnace), but it forms an almost infinite number of compounds. All living things contain carbon, and the element is therefore the basis or nucleus of organic chemistry. It is a decolorizing agent (bone-black serving best for this purpose) and a great absorber of gases, for which reason it is used in hospitals. It burns at a low temperature, but without flame (unless it contains gases), glowing and uniting with oxygen to form carbon dioxid. $C + \widehat{2O} = \widehat{CO_2}$. At a high temperature it removes oxygen from oxids of metals, acting thus as a *reducing agent*. Iron ores and many others are reduced in this way by carbon. $Fe_3O_4 + 4C = 3Fe + \widehat{4CO}$. $Fe_2O_3 + 3C = 2Fe + \widehat{3CO}$. The ore of iron, Fe_3O_4 or Fe_2O_3 , is the compound which gives up its oxygen to the carbon, and is called an oxidizing agent.

80. An Oxidizing Agent is a substance which, having oxygen, gives it up to a reducing agent.

81. A Reducing Agent is a substance which takes oxygen from an oxidizing agent. It is also called a deoxidizing agent. The above are restricted definitions sufficient for the present.

82. Tests.—The fact that carbon in any form burns in oxygen or air and forms carbon dioxid, which is easily tested (Chap. XXI), is a sufficient test for the element. In its compounds, like the hydrocarbons, it forms the same product, CO_2 .

Exp. 41.—Fill an ignition tube not over a third full of an intimate mixture of copper oxid, CuO , 7 parts by weight, and powdered charcoal, C , 1 part. Heat the substance, and look for any red glow in the tube. The whole mixture should be affected. When this is done, pour the contents into an evaporating dish, examine the product, and to a little of it add a

few drops of nitric acid, noting the color of the fumes and of the liquid. In this experiment the carbon has combined with the oxygen of CuO and reduced the latter, leaving Cu . $\text{CuO} + \text{C} = \text{Cu} + \text{CO}$. The nitric acid was used only to test for copper. $3\text{Cu} + 8\text{HNO}_3 = 3\text{Cu}(\text{NO}_3)_2 + 4\text{H}_2\text{O} + 2\text{NO}$. The copper nitrate formed is green, and the NO (which is colorless) unites with O in the air to form NO_2 , which is red.

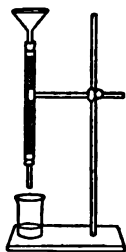


FIG. 38.

Exp. 42. — Put about 10% of powdered bone-black into a test tube, and pour over it 15 or 20^{cc} of a solution of cochineal, litmus, or anilin coloring matter, shake it well and filter. If the color is not all taken out, try it again. The experiment may be done as shown in Fig. 38 without shaking the solution.

Exp. 43. — As in Exp. 42, shake up with powdered charcoal some hydrogen sulfid solution, H_2S , in a test tube (Fig. 39), and filter, noting the odor of the filtrate, and that of the original H_2S .

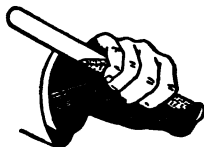


FIG. 39.

Exp. 44. — Place on thick paper a well dried piece of phosphorus the size of a pea. Sprinkle it lightly with bone-black. After a while it should take fire spontaneously. The carbon absorbs oxygen from the air and condenses it in its pores (an action called *occlusion*). Heat is also absorbed. Some of the occluded oxygen comes in contact with the phosphorus and sets it on fire. Care must be taken to have all the phosphorus burned up.

83. Uses. — The applications of amorphous carbon are very many. Charcoal and coal are used for heating purposes, reducing agents, decolorizers, printers' ink, etc. Its permanence is shown in well-preserved printing in books more than 400 years old. Millions of tons of iron and of other metals are reduced from their ores with coke and charcoal, and millions of pounds of sugar are refined by filtering through bone-black.

CHAPTER VIII.

COMBUSTION AND FLAME.

84. “Human culture began with fire.” The Egyptians, Greeks, Persians, and Romans had public fires in all their villages, and these were kept burning night and day. Mexicans and Peruvians had fires on large pyramids. Among the Romans nothing unholy was put into the fire, no wicked deed was done in the presence of fire, and swearing by the hearth was the most sacred oath. Fire-worship has been very common among most early peoples, and it is doubtful if any savage tribe exists which is ignorant of fire.

85. History.—The phlogiston theory (Becher, 1669, Stahl, 1702) assumed that when substances burned, a subtle principle called phlogiston was set free. Those which burned best contained most of it. Fire was escaping phlogiston. Sulfur and charcoal had little else than this principle, which was expelled when they burned. Iron, lead, etc., when heated left a residue, which was called a *calx*, after phlogiston had escaped. Heating a *calx* with a substance rich in this principle restored the original substance with its phlogiston. Thus iron was a compound of *calx* (we call it iron oxid) and phlogiston. Sulfur was a compound of the latter with sulfuric acid. Such ideas prevailed till Lavoisier explained combustion.

86. Combustion is rapid chemical union attended with light and heat. *Flame* is not a substance, but only a phenomenon accompanying such union. There must be two substances in combustion: 1. Something to unite, — a combustible. 2. Something for this to unite with, — a supporter

of combustion. There is another condition necessary, *viz.*, a temperature sufficiently high for the union to take place. *Fire* is a term nearly synonymous with *combustion*.

87. Flame indicates the combustion of a gas. Solids in burning simply glow, but do not burn with flame. Most flames have essentially the same structure. The candle, kerosene, gas, and Bunsen flames, and great conflagrations, have all practically the same parts, and the reactions are quite similar in all. Two of these, the Bunsen and the candle, will suffice for comparison and study.

88. Structure.—The general form of the entire flame is like a cone, or a double cone with the widest part above the base. This is broadly true of both candle and Bunsen flames. Each is made up of three separate cones

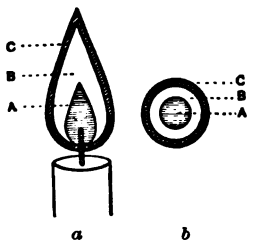


FIG. 40. — Candle flame. *a*, vertical section; *b*, horizontal section.



FIG. 41. — Bunsen flame.

or envelopes. The interior cone of the candle flame (*A*, Fig. 40) is dark or black, of the typical Bunsen it is green. It gives no light. The second or yellow cone of the candle, *B*, is the light-giving portion. In the Bunsen it is pale blue.

The outer cone, *C*, is scarcely discernible in the candle, except at the base, where it is deep blue. This outer mantle can be seen best in a dark room, or by holding it in front of a black-board, moving it slightly meanwhile, or by covering the rest of the flame with a knife-blade held between it and

the eye. The outer mantle of the Bunsen flame is usually a deeper blue than the second cone. The shadow cast on white paper by a flame when placed in direct sunlight shows the parts to the best advantage.

Exp. 45. — Examine a candle flame, noting all the parts, with colors of each, and make a drawing to illustrate. Hold it in front of a black-board to see the outer portion, also place it in direct sunlight, and examine the shadow cast on white paper.

Exp. 46. — (1) Examine, as before, a Bunsen flame, and make a drawing. (2) Hold a small splint across the lower part of the flame just above the lamp for a moment. Remove it, and note where it is burned. (3) Hold it just above the inner cone, and note again. (4) Draw the end of a glass tube to a capillary, put the other end in the inner cone just above the lamp tube, and try to light the gas at the capillary end. (5) Gradually raise the other end till it is in the second cone above the inner, and note the effect. (6) See whether there is any inward suction or outward pressure of air or gas at the lower orifices. (7) Examine a dissected burner, *i.e.*, one with the tube removed; notice the openings for gas, and light the gas.

89. Temperatures. — Recent experiments of Lewes indicate that the second cone is hotter than either of the others, and the outer one stands next. The temperature of the inner cone of the Bunsen flame varies from about 55° at the lower part to 1100° at the upper. At *B*, the hottest part (just above the boundary of the smallest cone), it is not far from 1500° . A few temperatures are given for comparison from Moissan's experiments. A low red heat just visible, *e.g.*, when iron is heated, indicates 450° . Fe_3O_4 melts at 2250° , CaO at 3000° , C volatilizes at 3500° , which is the temperature of the electric arc, negative pole. The oxy-hydrogen flame is some 2000° , hot enough to melt Pt or SiO_2 .

Exp. 47. — Press quickly down on a Bunsen flame with a piece of cardboard or white paper, and remove quickly before it is set afire. Note that the part representing the second cone is charred most, proving which cone is hottest.

90. Light. — No part of the Bunsen flame gives much light. In the candle flame light is confined to the second cone. If the openings at the base of a Bunsen burner are closed, the second cone gives light, as in the candle. The ordinary or fish-tail gas flame has the same three parts as the others, but flattened out, and the light-giving part is still the middle one.

Exp. 48. — (1) Sprinkle the slightest pinch of charcoal dust into a Bunsen flame, or rub together two pieces of charcoal near the lower orifices so that minute particles may be carried up into the flame. Note the effect, and explain the light of flame. (2) Try reduced iron, or file a nail over the flame. (3) Stir up the dust near a Bunsen flame. (4) Close the orifices at the base, and explain the result. (5) Set fire to a small piece of charcoal. See whether it flames up or glows.

91. Combustion in Flame. — No combustion takes place in the inner cone of either the candle or the Bunsen flame. This cone therefore cannot properly be called a flame. Combustion is most complete and general in the second cone, though it was formerly supposed that it was in the outer mantle. In the thin outer cone there is also combustion, but not as perfect as in the second. Either compression or rarefaction of the air is likely to make combustion less perfect.



FIG. 42.

Exp. 49. — Run a pin through a match near the phosphorus end, and put the long end into a burner (Fig. 42). Turn on the gas and light it above the match.

92. Kindling Temperature. — When carbon, sulfur, hydrogen, etc., were burned, each had to be set on fire or kindled, *i.e.*, the temperature had to be raised to a given degree before they would burn. This is called the *kindling*

temperature, and it varies for each substance. Below that point the given substance will not burn, but at that temperature it takes fire spontaneously in presence of a supporter of combustion. Phosphorus has a low kindling point, while that of carbon is considerably higher, and iron is higher still. Substances may be made to burn under water, and flames may be frozen out by cooling below the kindling temperature.

Spontaneous combustion ensues whenever there is a mixture of a combustible with a supporter, at the kindling temperature. In cotton or woolen rags saturated with oil, the oil absorbs

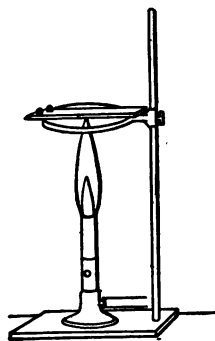


FIG. 43.

oxygen from the air, sometimes fast enough to ignite spontaneously the cloth and any combustible thing in contact with it.

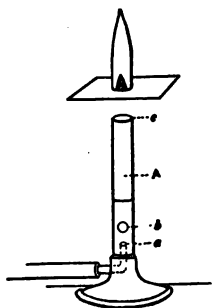


FIG. 44. — Bunsen burner. *A*, tube for mixing gas and air; *a*, where gas enters; *b*, where air enters; *c*, where gas burns.

Exp. 50. — Place on one end of a piece of iron (say 1" × 10") a piece of phosphorus and one of sulfur side by side, and heat the other end or the middle of the iron (Fig. 43). Note which of the elements first takes fire.

Exp. 51. — (1) Light a Bunsen jet, and press down with a fine wire gauze to 3 or 4^{cm} above the burner. (2) Extinguish, then relight the gas above the gauze (Fig. 44), and gradually lift the gauze till the gas will not burn. (3) Again light the gas above the gauze, and hold another gauze above the flame, so as to confine it above and below.

93. Explanation. — We are now ready to explain the phenomena of the combustion of flame. A candle consists

of hydrocarbons (compounds of C and H) rich in carbon. When the wick is lighted the heat melts these, giving liquid hydrocarbons, which are drawn up by capillarity through the minute tubes of which the wick is composed. The heat vaporizes the liquid, and diffuses the gas to the outer limit of the flame. Oxygen of the air diffuses inward through the first and second cones, and at the high temperature combines with the hydrogen and carbon to form H_2O , CO_2 , etc. When for any reason not enough O is present, or there is too low a temperature, CO may form, and some H, CH_4 , C, etc., be left unburned. The oxygen does not penetrate into the interior cone, neither is the temperature high enough there to promote combustion. The reason of the low temperature at this point is the absence of oxygen, and also, in small part at least, the formation here of other compounds, such as acetylene, C_2H_2 , which absorb rather than evolve heat in their formation. This absorption of heat cools the surrounding gas, so that even gunpowder, which carries its oxygen with it, would not burn. The inner cone then may be regarded as a gas factory. This gas diffusing outward meets oxygen, burns most completely, and gives the hottest flame in the second cone. In the outer mantle combustion continues, but is less complete than in the second. The yellow light is mainly caused by the incandescence or glowing of small particles of the solid carbon set free from its compounds. A gas, lamp, or candle flame often smokes, *i.e.*, throws off unburned carbon, because not enough oxygen is present. Why does a Bunsen flame give no light? Air is drawn in at the bottom, and oxygen mixes with the gas in the tube, so that when it burns at the top there is a complete mixture of the combustible

gas and the supporter, oxygen, and both the hydrogen and the carbon of the compounds burn together. Carbon is not set free and there is no chance for it to glow, hence there is no light. Close the air holes, and the case is like that of the candle or the lamp flame. The hydrogen of the compounds (*e.g.*, C_2H_2 , C_2H_4) burns first, sets free for a moment the carbon atoms, and during that moment the atoms of solid carbon glow before or at the time they combine with oxygen. Light, then, is due to the incandescence of solids.

94. Oxidizing and Reducing Flames. — As the inner cone contains no oxygen, and the heat at its very top is considerable, it will take oxygen from any substance containing it, *e.g.*, an oxid. A mouth blow-pipe and attachment (Figs. 45 and 46) are used for this purpose. If a little lead oxid, PbO , is put on some charcoal and the inner flame blown against it, the gas takes the oxygen from the PbO , leaving Pb and forming CO , H_2O , etc. A type of the reaction is: $3PbO + \widetilde{C_2H_2} = 3Pb + 2\widetilde{CO} + \widetilde{H_2O}$. The inner flame is therefore called the reducing flame.

The middle flame contains oxygen, and will impart it to elements to be oxidized. If this flame is blown against a piece of lead, it gives its oxygen to the metal and forms yellow lead oxid. $Pb + O = PbO$. The middle flame is therefore called the oxidizing flame.



FIG. 45.

Exp. 52. — By using the mouth blow-pipe (Fig. 45), blow the inner flame steadily for some time against some PbO in the hollow of a piece of charcoal (Fig. 46). Try to cut or crush the metal obtained.

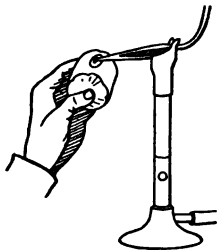


FIG. 46.

Exp. 53. — Blow the outer flame with the blow-pipe steadily and continuously against a piece of lead placed in the charcoal (Fig. 46). Note the color of any fumes rising, and the color of the coating on the charcoal.

95. Combustibles and Supporters. — Carbon, phosphorus, etc., burn in oxygen, hence the former are known as combustible

substances, the latter is a supporter of combustion. If we have two gases like hydrogen and oxygen, which is the combustible and which the supporter? If H burns in O, evidently H is the combustible. Will oxygen burn in hydrogen? If so, then O is the combustible and H the supporter. Experiments show that O will burn in H as well as H in O, the product in both cases being H_2O . Oxygen is the most common supporter of combustion; hydrogen and carbon, or compounds of them, are the more usual combustibles. But these are not all. Hydrogen, antimony, copper, etc., burn in chlorin, phosphorus burns in bromin, etc.

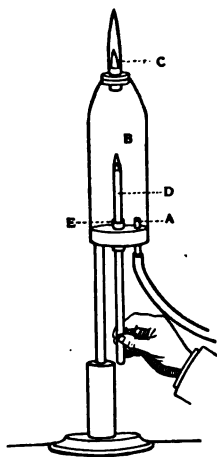


FIG. 47. — Oxygen burning in gas. A, where gas enters; B, chamber filled with gas; C, burning of gas in air; D, tube for entrance of air; E, where air burns on removing D.

Carbon dioxide, nitrogen, etc., are non-supporters of combustion, hence they may be used to extinguish fires. The former is often so used, especially in mines and fires in a closed building, where little oxygen can enter. CO_2 is found to exert a more powerful extinctive effect than N. There must be a certain per cent of a supporter or a combustible in order to produce flame. It is possible to have so small a per cent of hydrogen mixed with air, or so small a proportion of air, that there will be no union. If a little CO_2 is mixed with H and O the two latter will combine; but not if too much CO_2 is used. 20% of CO_2 prevents the combustion of C in air.

Exp. 54. — Fit a cork with two holes (one having a short glass tube, the other a metallic tube) to the large end of a

lamp chimney. To the upper end of the chimney fit a cork with one hole through which passes a short metallic tube. Connect the glass tube by a rubber to a gas jet. Turn on the gas, and after a minute light it at the top of the chimney. Pass a metal tube up through the two metal tubes in the chimney, and then withdraw it. The air will be drawn in, and oxygen will burn in the gas (Fig. 47).

96. Explosion.—If a lighted match is brought to a mixture of hydrogen and oxygen, an explosion ensues. The flame brought to the edge of the mixture instantly spreads through the whole, and combination takes place in all parts at once. The great heat liberated by the sudden union of the whole volume of gas, expands the product to many times its original volume, and it almost as suddenly contracts. The sudden expansion forces everything else aside, and if the gases are confined, breaks the confining walls, producing an explosion. In the contraction which follows, the molecules roll over each other and rush back, and thus there are two sounds following in rapid succession. Rapid combustion in a confined space makes an explosion.

97. The Most Explosive Mixture of hydrogen and oxygen is evidently 2 volumes of the former to one of the latter, since that is the proportion in which the two gases unite. What is the most explosive mixture of marsh gas, CH_4 , and air? First write the equation for marsh gas and oxygen. $\text{CH}_4 + 4\text{O} = \text{CO}_2 + 2\text{H}_2\text{O}$. Two volumes of CH_4 require 4 of O (Chap. XIX), hence the proportion is, marsh gas : oxygen : : 1 : 2. Since oxygen is a fifth of air by volume, marsh gas : air : : 1 : 10, and there should be 10 volumes of air to 1 of CH_4 . What is the most explosive mixture of acetylene, C_2H_2 , and air? Of C_2H_4 and oxygen? Of CO and air?

Most mine explosions are caused by CH_4 , "fire damp," escaping from the coal and mixing with

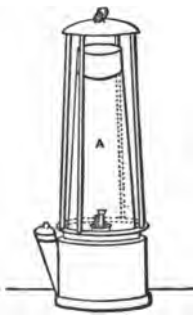


FIG. 48.

the air. The miner brings a naked flame to the mixture and explosion

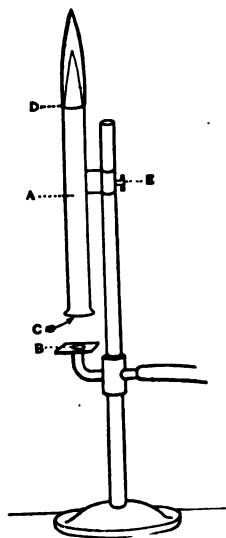


FIG. 49.

results. The Davy miner's lamp (Fig. 48), or a similar one, prevents an explosion. A surrounding wire cools the gas outside the lamp below its kindling point, even though inside it is burning vigorously, but a slight increase in the size of the flame, or a change in color, warns the miner of danger, and that part of the mine is left till it can be aerated. Very fine coal dust absorbs oxygen and is said to be the cause of some explosions in mines. Explosions in grist mills, soap factories, etc., occur sometimes as a result of the absorptive action of fine flour and of soap.

Exp. 55. — Slowly turn down the burning gas of a Bunsen lamp, and notice that it suddenly explodes, and expires at the top, but now burns at the base. Then turn it on and light it at the top. Notice that it now burns at both ends. As the gas was gradually turned off, more air became mixed with it, until there was the right proportion of each gas for an explosion. Fig. 49 shows the same thing.

Light the gas at the top, *D*, when the tube *A* covers the jet *B*. Then gradually raise the tube *A*. Air enters at *C* and mixes with the gas. At a certain point there is the same explosion as with the lamp, and the flame then burns at *B*.

CHAPTER IX.

ELECTRO-CHEMISTRY.

I. ELECTRO-CHEMICAL RELATION OF ELEMENTS.

98. Of some 75 elements known to chemists, about half are so rare as not to need consideration here. Elements are divided for convenience into two classes — metals and non-metals. The greater part are metals, there being about 15 or 16 that are usually classed as non-metallic, but the division line is not a sharp one. Only about two dozen metallic elements are abundant, and half that number of non-metals.

99. History. — Berzelius, a Swede, in 1818, first made this division of elements into the two classes which he called metals and metaloids. We shall here repeat some of his experiments.

100. Results. — Berzelius dissolved silver in nitric acid, HNO_3 , and thus made a solution of silver nitrate, AgNO_3 . Then he found that the silver could be recovered by putting a piece of copper into the solution. The copper dissolved as copper nitrate, $\text{Cu}(\text{NO}_3)_2$, and threw the silver out of solution, *i.e.*, precipitated it. He also found that lead or zinc would take the place of silver, just as the copper had done. From this it appeared that either copper, lead, or zinc had stronger affinity for nitric acid than silver had. He also made a solution of copper nitrate, by dissolving copper in nitric acid, and found that silver would not replace the copper, but that lead or zinc would do so, pre-

precipitating the copper and forming lead nitrate, $\text{Pb}(\text{NO}_3)_2$, or zinc nitrate, $\text{Zn}(\text{NO}_3)_2$. From a solution of lead nitrate, zinc precipitated lead, but neither silver nor copper had this effect; and in a solution of zinc nitrate, none of the other metals had any effect.

These experiments showed that zinc had the strongest affinity for nitric acid (or for the NO_3 radical), lead had the next strongest, then copper and lastly silver, which had least of all. He tried the other metals, and also experimented on them with other acids, as sulfuric, H_2SO_4 , and hydrochloric, HCl . There was not always exactly the same order of affinity of the metals for different acids, but as a result of a large number of experiments (some of which, especially with the non-metals, were of a kind different from those given here), the accompanying table (p. 66) of relative affinities was made out. In general the most metallic elements have the strongest affinity for acids, and those most non-metallic have the weakest. Those with greatest affinity for acid Berzelius called *electro-positive*, with reference to the others, and those with least affinity *electro-negative*. We often call them positive or plus elements, — a term nearly synonymous with *metals*, — and *negative*, *minus*, or *non-metallic*. Those elements farthest apart, *i.e.*, most metallic and most non-metallic, have in general greatest affinity for each other, while those near together have least. It will be seen that non-metals are positive or negative with reference to each other, and metals are also; *e.g.*, nitrogen is positive to oxygen, and potassium to sodium.

Exp. 56. — Put a ten-cent coin or other silver piece into an evaporating dish, and pour over it 1 or 2^{cc} of nitric acid, HNO_3 . Warm it, noting the color of the fumes, and, very cautiously, their odor, also the

color of the liquid. When the action stops, add 10°C H_2O , take out the coin, and pour the liquid into a test tube, then put in a bright copper wire (Fig. 50). Leave it 10 to 30 minutes and watch the result. The equation for dissolving the silver is $3\text{Ag} + 4\text{HNO}_3 = 3\text{AgNO}_3 + 2\text{H}_2\text{O} + \widetilde{\text{NO}}$ (not, as might be supposed $\text{Ag} + \text{HNO}_3 = \text{AgNO}_3 + \widetilde{\text{H}}$, Chap. V). The equation for the withdrawal of Ag from solution and substitution of Cu is $2\text{AgNO}_3 + \text{Cu} = \text{Cu}(\text{NO}_3)_2 + 2\text{Ag}$.



FIG. 50.

Exp. 57. — This experiment is done like the other except that a strip of copper or a piece of copper wire is dissolved in place of silver, less HNO_3 is used, and the acid is not warmed. When the action stops and water is added, warm the latter slightly and put in a bright piece of lead wire.

Exp. 58. — Dissolve a piece of lead in dilute HNO_3 (about 10°C , half water and half acid), and heat it till action begins, then remove the lamp. When the action stops, add H_2O , take out the lead, pour the liquid into a tube, and place in it a zinc wire.

101. Metals are usually heavy solids, good conductors of heat and electricity, malleable and ductile; they form alloys with each other, are electro-positive, and have a metallic lustre, — a property of reflecting light different from non-metals. Non-metals are either solid, liquid, or gaseous, and are usually non-conductors of electricity; they form physical solutions, are electro-negative, and have different lustres, which are not metallic. The *lustre* of substances can be observed by comparing freshly cut or untarnished pieces of lead, iron, silver, copper, or gold with glass, wood, paper, resin, etc. It must not be confounded with color. Gold, silver, and copper have different colors, but all have the same lustre.

Now this classification into metals and non-metals, although there is no absolutely sharp division line, is an important one in the bearing it has on the three great classes of chemical compounds, *acids*, *bases*, and *salts*. Metals, when combined with hydrogen and oxygen, form bases; non-metals with the same elements form acids.

102. Radicals. — A radical is a group of elements which has no existence as a separate substance, but enters into composition with other elements or radicals, or else breaks up. When silver reacts with nitric acid, HNO_3 ,

the nitrate radical, NO_3 , separates from the hydrogen and unites with the silver, forming AgNO_3 . If lead nitrate, $\text{Pb}(\text{NO}_3)_2$, is heated, the radical breaks up and forms other substances, but there is no such compound as NO_3 . The part of the symbol following the metal (or hydrogen), is usually a negative radical. SO_4 (from H_2SO_4) is the sulfate radical, PO_4 is the phosphate radical, etc. NH_4 (ammonium) is a positive radical, the only metallic one we shall meet at present. It is found in compounds like NH_4Cl , ammonium chlorid, $(\text{NH}_4)_2\text{SO}_4$, ammonium sulfate. OH is the hydroxid radical. Its compounds result from substituting a metal for half of the hydrogen in H_2O , as KOH , potassium hydroxid or hydrate, NH_4OH , ammonium hydrate or hydroxid.

Negative or Non-Metallic Elements. Acid-Forming with H (usually OH).	—
	Oxygen
	Sulfur
	Nitrogen
	Fluorin
	Chlorin
	Bromin
	Iodin
	Phosphorus
	Arsenic
	Chromium
	Boron
	Carbon
	Antimony
	Silicon
	Hydrogen
	Gold
Positive or Metallic Elements. Base-Forming with OH.	Platinum
	Mercury
	Silver
	Copper
	Bismuth
	Tin
	Cadmium
	Cobalt
	Nickel
	Lead
	Iron
	Zinc
	Manganese
	Aluminum
	Magnesium
	Calcium
	Strontium
	Barium
	Sodium
	Potassium
	+

103. Writing Symbols. — In our elementary work we shall usually find metals are combined with non-metals or with non-metallic radicals, as in KCl , NaNO_3 , but there are many exceptions, as N_2O , P_2O_5 . It is customary to write the positive or metallic part of a symbol first and the negative last, but this rule is not strictly adhered to, and a symbol written CO_3Ca means the same as CaCO_3 ; still it is better for beginners to follow the rule. Oxygen, if any is present, is written last. If two metals occur, the more positive is placed first, as Na_2AlO_3 . Arrange these: IAg , O_4SMg , CrO_4Pb , O_4FeP , CNa_2O_3 , HgNO_3 .

104. Explanation of Table. — In the accompanying table the elements most electro-negative are at the top, and those most electro-posi-

tive at the bottom. The most negative of all is oxygen, followed by several which are constituents of the strongest acids, as H_2SO_4 , HNO_3 , HF , HCl . The two at the positive end of the list, K and Na , are most metallic (or basic). We have seen that they do not need acids to dissolve them, but are so strong as to decompose water with violence. Hydrogen is intermediate in the list. It is a constituent of acids, of bases, and of the neutral compound water. Oxygen is also a constituent of bases, of most acids, and of many salts.

II. ELECTROLYSIS.

105. Since the last year of the eighteenth century, when water was decomposed by electrolysis, the electric current has become more and more a factor in chemical experiments. Many elements have been discovered by its use, several large chemical industries have lately been built up, and the prospect is that in future electricity will be employed for chemical manufacture on a far larger scale than it is at present.

106. History.—Water was electrolyzed in 1800 by Nicholson and Carlisle. In 1807 Davy decomposed, from the melted substances, NaOH and KOH —before then regarded as elements—and thus discovered sodium and potassium. In 1808 he isolated in the same way Ba , Sr , Ca .

107. Water is decomposed into its elements by a current of electricity. At the negative electrode (—, Fig. 51), there collects the plus element, H , and at the positive electrode (+, Fig. 51), the minus element, O . The equation is $\text{H}_2\text{O} = 2\widetilde{\text{H}} + \widetilde{\text{O}}$. It is noted that the volume of the hydrogen is twice that of the oxygen, though if the two gases were to be weighed the oxygen would be eight times the weight of the hydrogen, since, volume for volume, the former weighs sixteen times the latter.

108. Salts also can be electrolyzed. To electrolyze a salt like sodium carbonate, Na_2CO_3 , make a strong solution and connect it with a battery. At the minus electrode there will be liberated minute particles of the metal sodium, while at the plus electrode the negative radical appears. $\text{Na}_2\text{CO}_3 = 2\text{Na} + \text{CO}_3$. But Na, in contact with the solvent water, at once reacts with it and forms NaOH, setting hydrogen free. $\text{Na} + \text{HOH} = \text{NaOH} + \text{H}$. The CO_3 radical, as it cannot exist alone, at once breaks up into CO_2 and O. $\text{CO}_3 = \widetilde{\text{CO}_2} + \widetilde{\text{O}}$. CO_2 combines (in part at least) with the solvent water. $\widetilde{\text{CO}_2} + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$. Thus at the minus electrode would be formed a base, NaOH, and H, and at the plus electrode an acid, H_2CO_3 , and O. We see from this that a salt decomposes into an acid and a base. In Chap. XIII we see how the reverse action takes place, an acid and a base combining to form a salt.

Exercises. — By aid of the following equations explain the steps in the electrolysis of the salt potassium sulfate, K_2SO_4 . (1) $\text{K}_2\text{SO}_4 = 2\text{K} + \text{SO}_4$; (2) $\text{K} + \text{H}_2\text{O} = \text{KOH} + \text{H}$; (3) $\text{SO}_4 = \text{SO}_3 + \widetilde{\text{O}}$; (4) $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$. See whether you can write the equations for the electrolysis of NaNO_3 . Of NaCl . These experiments show that metals unite with the elements of water to form bases, and that non-metals unite with them to form acids.

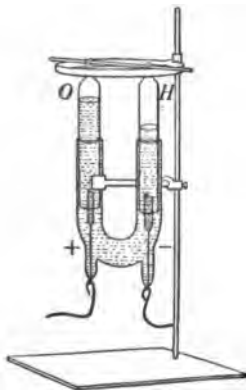


FIG. 51.

Wrong Theory. — Berzelius erroneously supposed that those oxids which collect at the minus electrode are charged with positive electricity, and those which collect at the plus electrode are charged with negative electricity, and that the two therefore attract each other. This was the origin of the binary or dual theory of compounds

so long held, according to which Na_2SO_4 was written $\text{Na}_2\text{O}\cdot\text{SO}_3$. NaNO_3 was $\text{Na}_2\text{O}\cdot\text{N}_2\text{O}_5$, each having a + and a — oxid, and other symbols were similar. This theory was abandoned about 1870.

109. Electrical Industries.—Many chemical industries have lately been modified by the use of electricity generated by the dynamo. White lead, which formerly took 3 to 6 months to prepare, now can be made in as many hours. Aluminum is reduced almost wholly by electricity, much copper is obtained by electrolyzing its salts, and the calcium carbide manufacture is an example of an industry created by the progress of electro-chemistry. At the high temperatures obtainable, carbon is found to reduce every metallic oxid, in the electrical furnace.

Exp. 59.—Arrange an electrolytic apparatus (Fig. 51), and connect the terminal wires with the wires of a Bunsen battery of several cells connected *in series* (see *Physics* for the construction and arrangement of batteries). Fill the apparatus with water in a trough, and acidulate the water with a few drops of H_2SO_4 , to facilitate conductivity. The terminal wire connected with the zinc is called the minus electrode (—, Fig. 51), that connected with carbon is the plus electrode (+). Each gas may finally be tested, one for H, the other for O.

CHAPTER X.

VALENCE

110. How are we to know whether to write the symbol of a given compound with 1, 2, 3, or 4 atoms of either of its elements? Shall we, *e.g.*, write the chlorid of magnesium Mg_2Cl , MgCl , MgCl_2 , MgCl_3 , or MgCl_4 ? One of these is right, the others are wrong. Heretofore we have simply memorized symbols. We shall now try to ascertain in what proportion the atoms of elements combine. This constitutes the study of *valence* or *quantivalence*.

111. History. — In 1834 Dumas showed that 1 atom of O had the same replacing value as 2 atoms of H, or 2 of Cl, and Liebig noticed that H and K had the same value, which was only a third that of Sb, but Frankland, 1852, first definitely stated the principle of valence, or the saturation capacity of elements. Kolbe, 1854, stated that lower stages of saturation sometimes existed, and Wurtz and Naquet established the double valence of some elements, 1864. Frankland's valence theory was accepted by chemists about 1860.

112. Explanation. — *The valence of an element is the combining or replacing value of its atom.*

The combining power of the hydrogen atom is the unit of valence, as this element has the smallest combining value. Its valence is said to be one. In the molecule whose symbol is HCl the chlorine atom has the same valence as the hydrogen, *viz.*, one. In the following symbols note the valence of each metallic (or first written) element: NaCl , CaCl_2 , BiCl_3 , CCl_4 . In NaCl it will

be seen that one atom of Na replaces one of H in HCl, or the Na atom has the same replacing value as H, *i.e.*, the valence of Na is one. If sodium and chlorine were brought together under suitable conditions to make them react, each atom of sodium would combine with one atom of chlorine: $\text{Na} + \widehat{\text{Cl}} = \text{NaCl}$. If sodium and hydrogen chlorid should react, one atom of sodium would displace one atom of hydrogen: $\text{Na} + \text{HCl} = \text{NaCl} + \widehat{\text{H}}$.

In magnesium chlorid, MgCl_2 , one atom of magnesium cannot combine with a single chlorine atom, but it selects two atoms. If the compound were to be formed from its elements, the equation would be: $\text{Mg} + 2\text{Cl} = \text{MgCl}_2$. If it could be formed by action of hydrogen chlorid on the metal, the equation would be $\text{Mg} + \left\{ \begin{smallmatrix} \text{HCl} \\ \text{HCl} \end{smallmatrix} \right\} = \text{Mg} \left\{ \begin{smallmatrix} \text{Cl} \\ \text{Cl} \end{smallmatrix} \right\} + \left\{ \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \right\}$, or $\text{Mg} + 2\text{HCl} = \text{MgCl}_2 + 2\widehat{\text{H}}$. The valence of Mg is therefore 2. In the chlorid of bismuth, BiCl_3 , the bismuth atom cannot combine with one or two chlorine atoms, but is not satisfied with less than three. Formed from the elements, the equation would be: $\text{Bi} + 3\widehat{\text{Cl}} = \text{BiCl}_3$. If made by the action of HCl: $\text{Bi} + 3\text{HCl} = \text{BiCl}_3 + 3\widehat{\text{H}}$. Hence the valence of bismuth is 3. Now carbon requires four atoms of Cl to satisfy its attraction, and carbon chlorid is CCl_4 . If the two elements could unite directly, what equation would represent it? If it could be got from C and HCl? The valence of carbon is 4. The reason for this selective action of different elements for a varying number of atoms is not known.

Exercises. — Any element which replaces hydrogen atom for atom, or any element which combines with hydrogen atom for atom, has a

valence of one, is said to be *univalent*, and is also called a *monad*. Thus the valence of chlorine in HCl is 1. Note the valence of each of these elements, which are united to H: HBr , HI , HF . Any element combining atom for atom with one of these elements, F, Cl, Br, I, is also a monad. Note the valence of the first written element in these: NaBr , KI , AgCl , AgI , NaF . Elements which require two of these atoms to make a molecule of a compound have their valence 2, and are called *bivalent* elements, or *dyads*, *e.g.*, calcium in CaBr_2 . Note and name the valence of these metals: CuCl_2 , HgI_2 , MgBr_2 . Write symbols for chlorids, bromids, iodids of these dyads: Cd, Fe, Ca, Sr. The elements whose atoms select three atoms of a monad are *trivalent*, or *triads*, or their valence is 3, *e.g.*, As in AsCl_3 . Write symbols of chlorids, bromids, and iodids of these triads: Sb, Bi, P, Fe, Cr, Al. A *tetrad*, or *tetravalent* element, has its valence 4. C and Si are the most important tetrads. A few elements are *pentads*, *i.e.*, their valence is 5, *e.g.*, P, Bi, Sb. Write symbols for their pentachlorids. A higher valence than 5 is rare, though *hexads* and *heptads* are known.

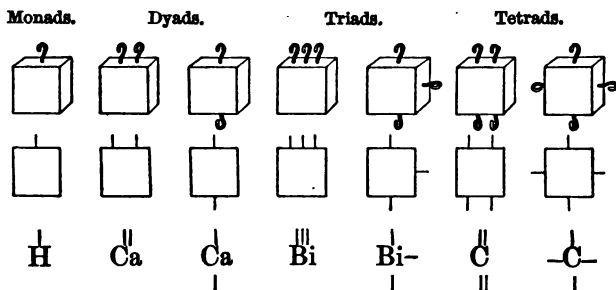
113. Double Valence.—Elements often have more than one valence, *e.g.*, P sometimes combines with 3, sometimes with 5 atoms of Cl. In the first case it is a triad, PCl_3 , in the second a pentad, PCl_5 . The iron atom under some conditions selects 2, under others 3 atoms of Cl, as FeCl_2 , FeCl_3 . These are called, respectively, *ferrous* and *ferric* chlorids. Sn takes 2 or 4; C 2 or 4; Hg 1 or 2. Write their chlorid symbols. Occasionally elements have a certain valence towards one element and a different one towards another, but usually varying conditions of formation govern this peculiarity. When hydrogen and oxygen combine to form water the molecule is H_2O , and oxygen is a dyad. This valence of oxygen must be regarded as invariable as that of hydrogen. It is the standard of valence for negative or non-metallic elements.

Exercises.—State the valence of the metals in each of these: FeO , CaO , Na_2O , K_2O , CuO , Ag_2O . A triad unites with a dyad as follows:

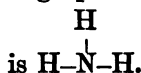
Fe_2O_3 (note that Fe is the triad). Write oxids for these triads: Al, Cr, N, P, Sb, Bi. In H_2S replace the hydrogen with these monads: K, Ag, Hg; with these dyads: Cu, Mn, Cd; with these triads: As, Sb, Bi. Each of the above united with S forms a metallic sulfid. If a monad unites with a triad, the symbols will be as follows: H_3P , Na_3As , H_3N . A dyad joins a triad as follows: Ca_3P_2 , Cu_3As_2 .

The valence of an element is often indicated by marks at the right and just above the symbol, as Ag', Pb'', Sb''', Si^{iv}, which indicate, respectively, a monad, dyad, triad, tetrad. Atoms are often pictured as having hooks or bonds to attach them to other atoms. Monads have one hook each, dyads have two hooks or bonds, triads three, tetrads four.

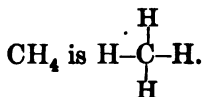
114. Representation.—The following are different devices for illustrating valence graphically, and are called graphic symbols:¹



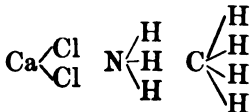
When atoms of these elements combine with others they are imagined to attach themselves by their hooks or bonds to those of the attracting element. The graphic symbol of a compound may be written by giving the elements with their respective bonds or hooks. NaCl is graphically written Na—Cl. CaCl_2 is Cl—Ca—Cl. NH_3



¹ For class use the first set are admirably illustrated by using cubical kindergarten blocks with small screw-eyes and hooks.



They may also be written,



Write graphic symbols for these, *carefully distinguishing between the atom and its bonds*: CuCl_2 , Na_2O , K_2S , H_3P , Fe_2O_3 , FeO , KBr , N_2O_3 , Cd''S'' .

115. Determination of Valence.—How may we determine the valence of an element from the symbol of one of its compounds? What, *e.g.*, is the valence of Mg in MgO ? O always has two bonds, and hence Mg must have the same number, as there is one atom of each in the symbol. To verify this, write the number of bonds above the element, with plus sign for that over the metal, and minus for the other, $\text{Mg}^{+2}\text{O}^{-2}$.

*In any symbol there must be as many plus bonds as minus.*¹ There must be no free (or unsaturated) bonds; in order to form a stable compound, all must be attached. This is imagined to explain why atoms of elements usually exist only in pairs, two hydrogen atoms, *e.g.*, attaching themselves together to form a stable molecule, $\text{H}-\text{H}$, or H_2 . Now HO is not a correct symbol, for this would leave one free bond, $\text{H}-\text{O}-$, which attracts another H atom to saturate it, as $\text{H}-\text{O}-\text{H}$, or H_2O . The valence of N in N_2O may be considered 1, $\text{N}_2^{+2}\text{O}^{-2}$, i.e., 1 oxygen atom with 2 bonds, is equivalent to 2 nitrogen atoms with 1 bond each. In N_2O_3 it is 3, since 3 atoms of O with 2 bonds each equal 6 bonds, $\text{N}_2\text{O}_3^{-6}$, and the 2 atoms of N must also have 6, $\text{N}_2\text{O}_3^{+6}$, and since 2 atoms have 6, 1 will have 3 bonds, $\text{N}_2^{+6}\text{O}_3^{-6}$, or N is here a triad.

Follow the above plan, write out all the work as there given, and verify the following symbols, giving the valence of: As in As_4O_6 , S in SO_2 and SO_3 , Hg in Hg_2O and HgO . The graphic symbol of N_2O is $\text{N}-\text{O}-\text{N}$. Of N_2O_3 it is $\left. \begin{array}{c} \text{N} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \\ \text{O} \end{array} \end{array} \right\}$, or $\text{O}=\text{N}-\text{O}-\text{N}=\text{O}$. Try to write that of each of the others.

¹ A plus element may not necessarily be a metal, so long as it is plus with reference to the element it is combined with.

116. Radicals as well as elements have valence. In the compound HNO_3 the NO_3 radical has valence 1, because it combines with 1 hydrogen atom. In KNO_3 and NaNO_3 , K and Na are each monads, as they replace H atom for atom, and the radical NO_3 is likewise univalent. Cu is a dyad, hence when it reacts with HNO_3 and displaces the H, it must displace 2 atoms, or combine with 2 NO_3 radicals, and the symbol of copper nitrate is $\text{Cu}(\text{NO}_3)_2$, as that of copper chlorid is CuCl_2 . Silver nitrate is AgNO_3 and lead nitrate is $\text{Pb}(\text{NO}_3)_2$, because the valence of Ag is 1 and of Pb is 2, while that of NO_3 is 1. Suppose Pb were to replace Ag in a solution of AgNO_3 , the equation would require twice as many AgNO_3 molecules as of Pb atoms. $\text{Pb} + 2\text{AgNO}_3 = \text{Pb}(\text{NO}_3)_2 + 2\text{Ag}$, or $\text{Pb} + \left\{ \begin{smallmatrix} \text{AgNO}_3 \\ \text{AgNO}_3 \end{smallmatrix} \right\} = \text{Pb} \left\{ \begin{smallmatrix} \text{NO}_3 \\ \text{NO}_3 \end{smallmatrix} \right\} + \left\{ \begin{smallmatrix} \text{Ag} \\ \text{Ag} \end{smallmatrix} \right\}$.

Exercises. — Bi is a triad, and hence its nitrate is $\text{Bi}(\text{NO}_3)_3$. Write symbols for nitrates of: K', Mg'', Na', Bi''', Fe''', Fe'', Hg', Hg''. Let M^{iv} be a metallic tetrad; write its nitrate.

In H_2SO_4 the SO_4 radical is united to 2 hydrogen atoms, and hence has valence 2. Potassium has the same replacing value, and hence the molecule of sulfate of potassium is K_2SO_4 , not KSO_4 . The radical NH_4 has the same replacing value as H, hence ammonium sulfate is $(\text{NH}_4)_2\text{SO}_4$. Zinc is a dyad, and so 1 atom replaces 2 of H. Zinc sulfate is ZnSO_4 . The reaction of zinc with sulfuric acid is: $\text{Zn} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + 2\text{H}$. Triad elements uniting with dyad radicals give symbols as follows: Al''' and $(\text{SO}_4)''$ is $\text{Al}_2(\text{SO}_4)_3$. Verification: $\text{Al}_2^{+6}(\text{SO}_4)_3^{-6}$. Write symbols for these, and *verify them*: Na' and SO_4 , $(\text{NH}_4)'$ and SO_4 , Ba'' and SO_4 , Mg'' and SO_4 , Fe'' and SO_4 , Fe''' and SO_4 , Cr''' and SO_4 .

In phosphoric acid, H_3PO_4 , it is evident that PO_4 is a triad. Replace the H with Na, and we have Na_3PO_4 . Why not NaPO_4 ? Write symbols for K' and PO_4 , Ag' and PO_4 , Ca'' and PO_4 , Ba'' and PO_4 , Mg'' and PO_4 . Triads replace 3 atoms of H, as FePO_4 , CrPO_4 . In silicic acid, H_4SiO_4 , what valence has the radical? Symbolize silicates of Na', Pb'', Ca'', Al'''.

The principle above given enables us to ascertain the valence of the middle element of a triad, *e.g.*, KClO_3 . The valence of K being 1, of O 2, we have $\text{K}^{\overset{+1}{\text{Cl}}\overset{-6}{\text{O}_3}}$. As there must be as many + as - bonds, Cl will have 5, as $\text{K}^{\overset{+1}{\text{Cl}}\overset{+5}{\text{O}_3}}$. Take $\text{Pb}(\text{NO}_3)_2$ to find the valence of N. $\text{Pb}(\text{NO}_3)_2 = \text{PbN}_2\text{O}_6$, $\text{Pb}^{\overset{+2}{\text{N}_2}\overset{-12}{\text{O}_6}}$. There are 10 bonds left for N_2 , or 5 for each N, $\text{Pb}^{\overset{+2}{\text{N}_2}\overset{+10}{\text{O}_6}}$. Find the valence of N in KNO_3 , in KNO_2 ; of P in Ag_3PO_4 , in $\text{Ca}_3(\text{PO}_4)_2$.

117. Table of Valence.—In the table below, students should become familiar with the valence of the main elements, and especially should memorize the radicals. It is indispensable before proceeding further in the subject, that they be able to apply everything in this chapter.

COMMON ELEMENTS AND RADICALS.

These are arranged according to the *usual* or the more stable valence. The valence of radicals does not vary, but that of many elements does.

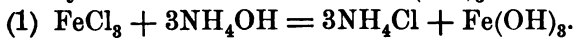
Metals and Positive Radicals.

Non-metals and Negative Radicals.

MONADS.	DYADS.	TRIADS.	TETRAADS.	MONADS.	DYADS.	TRIADS.	TETRAADS.
H	Mg	As	Pt	F	O	N	C
Na	Ca	Sb	Sn	Cl	S	P	Si
K	Sr	Bi		Br	SO_3	B	SiO_4
Ag	Ba	Au		I	SO_4	PO_2	
Hg	Pb	Fe		NO_2	CO_3	PO_3	
NH_4	Cu	Cr		NO_3	C_2O_4	PO_4	
CH_3	Cd	Al		ClO	$\text{C}_4\text{H}_4\text{O}_6$	AsO_3	
C_2H_5	Zn			ClO_2		AsO_4	
	Co			ClO_3			
	Ni			ClO_4			
	Hg			BrO_3			
	Sn			IO_3			
	Fe			$\text{C}_2\text{H}_3\text{O}_2$			

Exercises.—From the above table, the student should write the result of combination of several metals with non-metals or negative radicals (the metals always standing first in the symbol), as HF , H_2O , H_3N , H_4C , etc. Not every symbol that can be made in this way, however, represents a known compound.

118. Structural Symbols. — Molecules of compounds may differ in three ways: (1) In the *kind* of atoms they contain. CO_2 and CS_2 are composed of carbon combined in the one case with oxygen, in the other with sulfur. (2) In the number of atoms of the same elements. CO and CO_2 are composed of the same elements, but with different proportion of oxygen. Hence the properties of the two compounds in this case are very unlike, as they were in the previous one. (3) In the arrangement of atoms in the molecule, *i.e.*, in *molecular structure*. $\text{C}_2\text{H}_6\text{O}$ is the symbol for either methyl ether or ethyl alcohol, two compounds of very unlike properties. From their similarity of composition, it might be supposed that their properties would be the same, but such is not the case. How can this difference be explained, when an exact analysis shows that the percentage of carbon, hydrogen, and oxygen is the same in both? It is believed that the molecules are differently made up—that the carbon, hydrogen, and oxygen atoms have a different relation to each other in the ether from what they have in the alcohol. This difference of place (or of relation) of atoms in molecules constitutes *molecular structure*. Why is the symbol of ammonium hydroxid written NH_4OH and not NH_5O ? Experiments show that one-fifth of the hydrogen bears a relation to the rest of the compound different from that which the other four-fifths bear. If we add a solution of ferric chlorid, FeCl_3 , to the hydroxid, there are formed $\text{Fe}(\text{OH})_3$ and NH_4Cl , as:



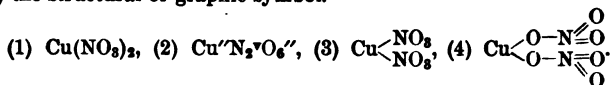
A similar reaction takes place with AlCl_3 , etc.

(2) $\text{AlCl}_3 + 3\text{NH}_4\text{OH} = 3\text{NH}_4\text{Cl} + \underbrace{\text{Al}(\text{OH})_3}.$ A large number of other salts give hydroxids with ammonium

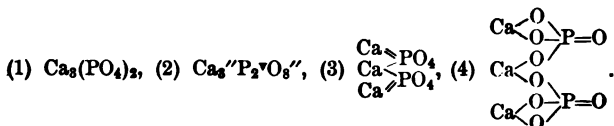
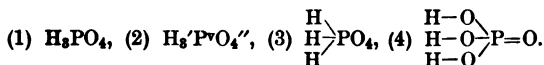
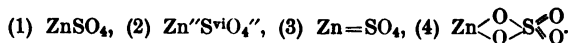
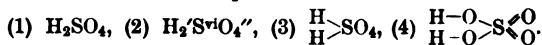
hydroxid. It will be seen in equation (1) that Fe combines with OH and displaces NH_4 , which unites with Cl, i.e., one of the H atoms is more strongly attached to the O atom than to the other four H atoms or to the N. As this occurs in a large number of reactions, the symbol is written NH_4OH instead of NH_5O . In the reactions, NH_4 unites with the negative element or radical, OH with the positive.

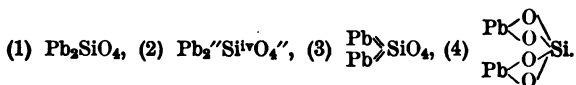
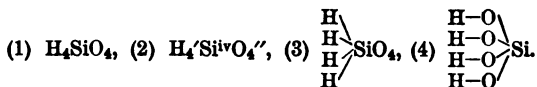
The efforts of chemists to picture molecular structure, or the relative position of atoms in the molecule, has led to structural symbols. The *empirical symbol* of nitric acid is HNO_3 . From the *valence symbol*, $\text{H}'\text{N}^{\vee}\text{O}_3''$, the valence of nitrogen is seen to be 5. A *semi-graphic symbol* is $\text{H}-\text{NO}_3$, but the complete *structural symbol* would be $\text{H}-\text{O}-\text{N}\equiv\overset{\text{O}}{\text{O}}$. The similarity to the symbol of water, $\text{H}-\text{O}-\text{H}$ (in which NO_2 takes the place of the last H), is seen by comparing the two.

In the following examples (1) is the common or empirical symbol, (2) is what may be called the valence symbol, (3) is the semi-graphic, and (4) the structural or graphic symbol.



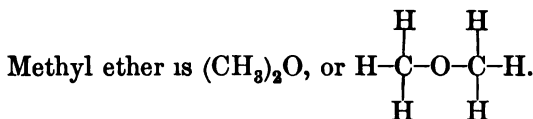
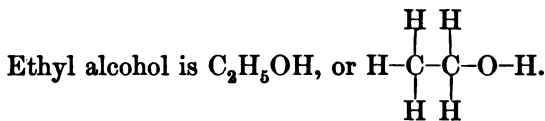
Note that Cu takes the place of 2H in two molecules of HNO_3 .





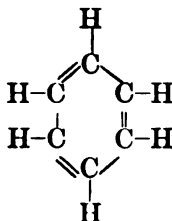
Exercises. — Write each of the following empirical symbols in the other three forms, as above: HClO , HClO_2 , HClO_3 , HClO_4 , H_2SO_3 , ZnSO_3 , H_3AsO_3 , H_3AsO_4 , H_2CO_3 , HNO_2 , $\text{Ca}(\text{ClO}_3)_2$, KNO_3 , $\text{Mg}_3(\text{PO}_3)_2$.

119. Isomerism. — Two or more compounds which have the same percentage composition of the same elements, but have different properties, are said to be isomeric. Ethyl alcohol and methyl ether, mentioned above, are examples, the latter being an isomer of the former. The symbols — empirical and structural — of each are as follows :



Substances like the above, in which the atoms are supposed to be placed differently in the molecule, are called *metameric*. The other main variety of isomerism (besides metamerism) is called *polymerism*. Polymers have the same percentage composition, but the molecule of the polymer is a multiple of the other. Benzene, C_6H_6 , is a polymer of acetylene, C_2H_2 . The percentage composition is the same in both cases, but the molecular

weight of the former is three times that of the latter. Structurally they are $\text{H}-\text{C}\equiv\text{C}-\text{H}$, and



To which class of isomeric substances do these belong: Starch, $\text{C}_6\text{H}_{10}\text{O}_5$, and cellulose, $(\text{C}_6\text{H}_{10}\text{O}_5)_x$? Ammonium cyanate, NH_4CNO , and urea, $(\text{NH}_2)_2\text{CO}$? The forms of isomerism have more application in organic chemistry than in inorganic.

120. Value. — While the study of valence is of great importance to beginners in the science — so much so that symbols, equations, etc., cannot be understood without a knowledge of the subject — yet the student must not attach the same value to the principles brought out in this chapter as he would, *e.g.*, to the law of definite weight, or the percentage composition of a substance. Valence is only a theory, structural symbols are pictured explanations, on the atomic theory, of results obtained by analysis — nothing more. They prove nothing, they simply illustrate.

CHAPTER XI.

EQUATIONS.

121. By a *reaction* is meant some definite chemical action, but the term is also used for an *equation*. An *equation stands for a reaction*. It represents a chemical experiment. Symbols and equations are the shorthand of chemistry. An equation gives the substances that are put together in an experiment, and those which are obtained as a result of it, together with the right proportions of those used, and of the ones obtained. The substances put together for a given experiment are called *factors*, and those obtained, *products*.

Before one can progress very far in chemical knowledge he must know how to write equations. To this end three things are essential: (1) To know the *factors* and their symbols; (2) To know the *products* and their symbols; (3) To balance the equation.

122. (1) Factors.—The first question one must ask himself is: *What substances did I put together to obtain the result?* In making sulfid of copper there were two factors, *viz.*, copper and sulfur. The first half of the equation would then be $\text{Cu} + \text{S} =$. Sometimes there is but a single factor, as when we obtain oxygen by heating red oxid of mercury, and the left-hand member of the equation then stands $\text{HgO} =$. Usually there are two factors, but there may be three or more in an experiment. When

only one or two substances take part in a reaction, a second or third is occasionally used for some purpose. In making oxygen from potassium chlorate, manganese dioxid was employed to distribute the heat and lower the temperature of dissociation of the chlorate, but we are not sure that it took part in the reaction, and hence it was neglected in writing the equation. If written at all it would have to appear on both sides unchanged. So in the preparation of hydrogen, water was employed, but was omitted in the equation, since its only use was to dissolve the zinc chlorid formed. In those experiments where water is employed solely as a solvent, it does not appear in the equation, except in those cases in which it combines with one of the products. *The symbols of the factors are always on the left of an equation.*

123. (2) Products. — *The products are the substances obtained as the result of an experiment.* These may be one or several. In the union of copper and sulfur there was one product, copper sulfid, CuS . The equation for this would be $\text{Cu} + \text{S} = \text{CuS}$. In the preparation of oxygen from mercuric oxid, two products, mercury and oxygen, are formed, and the equation is: $\text{HgO} = \text{Hg} + \text{O}$. In other cases, three or more substances result from a given reaction. *The symbols of the products of an experiment are always written on the right of the equation.* The equality sign separates factors from products. To determine the products of an experiment is by no means as easy as to find out the factors. At the outset we have to accept statements that such and such substances are formed, as when we are told that zinc chlorid results from pouring hydrogen chlorid on zinc. We might, however, have

tested the substance, as has repeatedly been done, and should have found the statement true.

In all cases where we are certain that a given reaction takes place, the products have been at some time ascertained, and in doing the experiments it is well to apply tests to as many as possible. But in a large number of cases, we have to accept the statements of those who have made careful analyses of the results. It thus becomes necessary at first to memorize the factors and the products. It is very easy, after a little practice, to calculate the most common reactions. If a double decomposition takes place, the metal (or positive part) of each compound joins itself to the non-metal (or negative part) of the other. On mixing the solutions of silver nitrate and sodium chlorid, there are formed sodium nitrate and silver chlorid: $\text{AgNO}_3 + \text{NaCl} = \text{AgCl} + \text{NaNO}_3$. Complete these: $\text{HgNO}_3 + \text{KCl} = ?$ $\text{NaOH} + \text{HCl} = ?$ $\text{KOH} + \text{HNO}_3 = ?$

Sometimes one metal sets free another from a compound, the former taking the place of the latter. In a solution of silver nitrate, copper will displace the silver, deposit it, and form copper nitrate: $\text{Cu} + 2\text{AgNO}_3 = \text{Cu}(\text{NO}_3)_2 + 2\text{Ag}$. Complete: $\text{Pb} + \text{Cu}(\text{NO}_3)_2 = ?$ $\text{Zn} + \text{Pb}(\text{NO}_3)_2 = ?$

Not every equation that can be written stands for a reaction. *It must be known whether a given reaction will take place, before an equation is written.* $2\text{NaCl} + \text{H}_2\text{O} = \text{Na}_2\text{O} + 2\text{HCl}$ is not correct, for on mixing the two substances there is no such reaction.

124. (3) Equality.—No equation is complete until it is balanced, but this should not be done till both factors and products are written. Since there is no loss or gain of matter, there must be just as many atoms of each element in the products as in the factors, only the atoms are differently combined. An equation means equality, and it expresses the law of *conservation*, viz., that there is no gain or loss in the transmutations of matter. In preparing hydrogen, the factors were $\text{Zn} + \text{HCl}$, and the products $\text{ZnCl}_2 + \text{H}$. Putting these into an equation, we have $\text{Zn} + \text{HCl} = \text{ZnCl}_2 + \widetilde{\text{H}}$. Now there is one atom of chlorin in the factors, and there are two atoms in the product. If this

were to stand, then *one* would equal *two*. To correct the absurdity, two atoms of Cl must be taken in the factors. We cannot write HCl_2 , as no such compound is known, but are compelled to take two molecules of HCl, in order to obtain

the two atoms, as: $\text{Zn} + \left\{ \begin{smallmatrix} \text{HCl} \\ \text{HCl} \end{smallmatrix} \right\} = \text{Zn} \begin{smallmatrix} \text{Cl} \\ \text{Cl} \end{smallmatrix} + \left\{ \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \right\}$, or

$\text{Zn} + 2\text{HCl} = \text{ZnCl}_2 + \widetilde{2\text{H}}$. Then two atoms of hydrogen are liberated from the two molecules of acid. This is only the expression in symbols of the fact that when zinc reacts with hydrogen chlorid, one atom of the former requires two molecules of the latter. All the millions of atoms of zinc in this experiment break up twice as many millions of molecules of hydrogen chlorid, unite with all the chlorin, and liberate all the hydrogen. The atoms of the latter unite in pairs to form hydrogen molecules.

In the experiment for preparing oxygen the factors and products are: $\text{KClO}_3 = \text{KCl} + \text{O}$, but in the factor are three atoms of oxygen, in the product but one. It should stand $\text{KClO}_3 = \text{KCl} + \widetilde{3\text{O}}$.

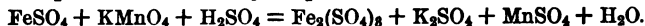
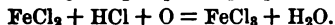
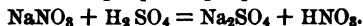
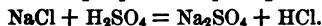
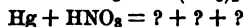
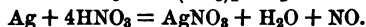
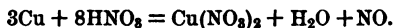
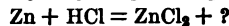
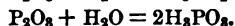
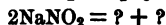
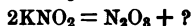
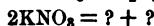
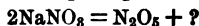
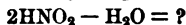
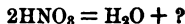
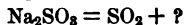
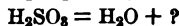
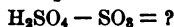
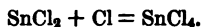
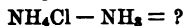
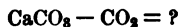
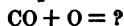
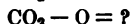
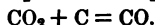
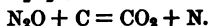
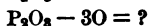
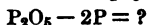
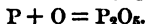
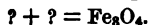
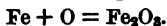
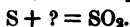
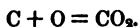
When sulfur burns in air, $\text{S} + \widetilde{\text{O}} = \widetilde{\text{SO}_2}$ expresses all except the proper proportion of the elements. There is O on the left and O_2 on the right of the equation. Correct the result in that case and in each of the following: $\text{C} + \widetilde{\text{O}} = \widetilde{\text{CO}_2}$. $\text{P} + \widetilde{\text{O}} = \text{P}_2\text{O}_5$. $\text{Fe} + \widetilde{\text{Cl}} = \text{FeCl}_3$. A brace above a symbol in an equation indicates a gas; one below shows a precipitate in a solution.

125. Variation of Equations.—There are very few equations that express all that takes place in an experiment. The most they can do is to give the general average of reactions. Differences of temperature, differences in strength of reagents, as well as different kinds of reagents, vary the results greatly. The action of nitric acid on metals is a good illustration. The general equation is $8\text{HNO}_3 + 3\text{M}'' = 3\text{M}(\text{NO}_3)_2 + 4\text{H}_2\text{O} + 2\text{NO}$. But this varies greatly with (1) temperature, (2) strength of acid, and (3) different metals. Often two equations are given to express

results at different temperatures. *Molecular equations*, as distinguished from *atomic equations*, contain no free atoms, but have all atoms combined as molecules. $\widetilde{\text{H}_2} + \widetilde{\text{O}} = \text{H}_2\text{O}$ is an atomic equation, $2\widetilde{\text{H}_2} + \widetilde{\text{O}_2} = 2\text{H}_2\text{O}$ is molecular. As the molecular composition of most elements is not known, it is better to write atomic equations.

Exercises. — To balance an equation begin at the left, count all the atoms of each element in the factors, and see whether it is the same for that element in the products. If not, make the two equal by prefixing coefficients.

Complete the following:



WHAT REACTIONS TAKE PLACE.¹

126. *In general those reactions take place in which the greatest amount of heat is liberated.* This was at one time regarded as the universal law governing reactions, but, while it is generally true, there have been found certain reactions in which heat is absorbed rather than liberated, as when hydrogen combines with iodine to form hydriodic acid. A few rules may be given which will materially aid the student in forecasting chemical reactions. Others will be considered in their appropriate places.

1. Berthollet's Law of Precipitation. — *An insoluble compound is formed whenever two solutions are mixed, one of which contains the positive or metallic part, and the other the negative or non-metallic part of an insoluble compound.* (See Chap. XIII.)

2. Berthollet's Law of Gases. — *If a gas can form by the reaction of two or more substances, it will always be liberated on mixing those substances.* Ammonium chlorid, NH_4Cl , mixed with calcium hydrate, $\text{Ca}(\text{OH})_2$, liberates ammonia, NH_3 .

3. Law of Neutralization. — *Acids have great affinity for bases, and bases for acids. The two react to form salts and water.* (See Chap. XIII.)

4. Metals. — *An acid will generally but not always dissolve a metal, if the salt formed is soluble, otherwise not.* Hydrochloric acid, HCl , dissolves zinc, as zinc

¹ It seems desirable to introduce this subject here, although parts of it can be best studied on review.

chlorid, ZnCl_2 , is soluble. HCl will not dissolve silver, for silver chlorid is insoluble. But acetic acid does not dissolve silver, though silver acetate is soluble.

5. Oxids and Carbonates.— *Acids will generally dissolve oxids and carbonates (and often other salts, as sulfids, etc.), if the salt naturally formed by such acid is soluble.* Nitric acid will dissolve lead oxid, carbonate, sulfid, etc.

6. Metals and Bases.— *Most metallic hydroxids are insoluble, and hence bases as a rule do not dissolve metals, etc.*

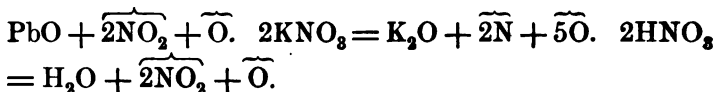
7. Acids and Salts.— *If an acid is strong enough to act upon a salt, another acid and another salt usually result.* H_2SO_4 acts on NaNO_3 to form HNO_3 and Na_2SO_4 .

8. Bases and Salts.— *If a base is strong enough to decompose a salt, another base and another salt usually result.* $\text{Ca}(\text{OH})_2$ with Na_2CO_3 forms NaOH and CaCO_3 .

9. Reduction.— *Reducing agents, like carbon, hydrogen, sodium, at a high temperature reduce oxids of metals to the metallic state.* Carbon reduces Fe_2O_3 to Fe by application of heat, and at a high enough temperature it will reduce every known oxid.

10. Soluble Gases.— Gases which dissolve in water usually form unstable compounds of indefinite composition. CO_2 and SO_2 dissolve readily in water, but do not form definite compounds and are unstable. Hence H_2CO_3 and H_2SO_3 are said not to have been isolated.

11. Heat.— Heat decomposes most *nitrates* into the metallic oxid, and NO_2 and O . The alkali and alkaline earth nitrates form the oxid, and N and O . $\text{Pb}(\text{NO}_3)_2 =$



Nitrites are reduced to oxids, and N and O; except AgNO_2 , HgNO_2 , $\text{Hg}(\text{NO}_2)_2$, which give the metal.

Chlorates form chlorids and O. $\text{KClO}_3 = \text{KCl} + \widetilde{3\text{O}}.$

Carbonates form the oxid and CO_2 . $\text{CaCO}_3 = \text{CaO} + \widetilde{\text{CO}_2}.$

Oxalates form the oxid, and CO_2 and CO. $\text{PbC}_2\text{O}_4 = \text{PbO} + \widetilde{\text{CO}_2} + \widetilde{\text{CO}}.$

Alkaline oxalates form carbonates and CO. $\text{Na}_2\text{C}_2\text{O}_4 = \text{Na}_2\text{CO}_3 + \widetilde{\text{CO}}.$

Sulfates form sometimes the oxid, and O and SO_2 ; again the oxid, and SO_3 and SO_2 .

Sulfates of the *alkali* and *alkaline earth* metals are not decomposed by heat.

Sulfites form oxids and SO_2 , or sulfates and sulfids.

CHAPTER XII.

ACIDS, BASES, SALTS.

127. Inorganic chemical compounds are divided into three great classes. While this division does not include all inorganic substances besides elements, it embraces the greater number of those compounds we shall have to deal with, and with which we come in daily contact. Having studied four typical elements and a few general principles of chemistry, we are now ready to learn some of the properties of these three classes, and how to distinguish them, and then to study some typical forms of each class, with their mode of preparation, their properties, uses, etc. These classes are *Acids*, *Bases*, and *Salts*.

128. History.—The word *oxygen* means *acid-former*. Lavoisier named the element, supposing it was found in all acids. What we call oxids he divided into two classes; one of these he called *acids*, the other *oxids*. Examples of the first class are SO_2 , SO_3 , CO_2 , N_2O_3 , P_2O_5 . These redden moist blue litmus, and we call them anhydrids, or non-metallic oxids. Davy, 1811, showed that *they combine with water and thus form acids*, and that hydrogen, not oxygen, is necessary for an acid. Some of the anhydrids are still erroneously called acids, as CO_2 , carbonic acid, SO_2 , sulfurous acid. The *oxids* of Lavoisier were compounds of metals with oxygen, and were not acid-formers. Combined with water they form bases.

ACIDS.

129. An Acid is a substance which has usually a sour taste, turns blue litmus¹ red, and reacts easily with a base, giv-

¹It has a similar action on many other vegetable coloring matters.

ing a salt and water ; it is composed of hydrogen—which can be replaced by a metal—and a non-metallic element or radical.

The three most common acids we shall meet with are hydrochloric, HCl ; nitric, HNO_3 ; sulfuric, H_2SO_4 . HCl is the formula of an acid because it consists of hydrogen united with a non-metallic element; also HNO_3 , which has hydrogen combined with a negative radical.

Most acids contain oxygen as well as hydrogen. The following six are exceptions: HCl , HBr , HI , HF , H_2S , HCN . Water, H_2O , ammonia, NH_3 , etc., though composed of hydrogen and a negative element, are exceptions to the general principle and are not acids.

Exercises.—From these symbols select the ones which stand for acids, and state your reason: $\text{H}_2\text{C}_2\text{O}_4$, CaCO_3 , NaOH , H_2S , HCN , BiCl_3 , H_2CO_3 , HBr , CaF_2 .

Complete the symbols for an acid in each of the following, and also give the name. The symbol and name of the first in the series is given and is a type for the others.

HCl , hydrochloric acid.

? Br, ? “

? I, ? “

? F, ? “

H_3PO_4 , phosphoric “

? As ? ? “

HNO_3 , nitric acid.

? Cl ? ? “

? Br ? ? “

? I ? ? “

H_3PO_3 , phosphorous acid.

? As ? ? “

130. The Names and Symbols of the following acids should be committed to memory by the student, as they represent most of the common salts; especially should the number of hydrogen atoms in each molecule be noted.

HCl , hydrochloric acid.

HBr , hydrobromic “

HI , hydriodic “

HF , hydrofluoric “

H_2CO_3 , carbonic “

HNO_2 , nitrous “

HNO_3 , nitric “

H_2SO_3 , sulfurous acid.

H_2SO_4 , sulfuric “

H_3PO_3 , phosphorous “

H_3PO_4 , phosphoric “

H_3AsO_3 , arsenious “

H_3AsO_4 , arsenic “

HClO_3 , chloric “

Exp. 60.—(1) Pour into an evaporating dish a few drops of HCl , add 4 or 5^{cc} H_2O , stir it, taste a drop from the stirring rod (Fig. 52). Dip the end of a strip of blue litmus paper into it. State results. (2) Rinse the evaporating dish, then put in a few drops HNO_3 and 5^{cc} H_2O , stir and test as before. (3) Test in like manner H_2SO_4 . What do these experiments teach you of acids?

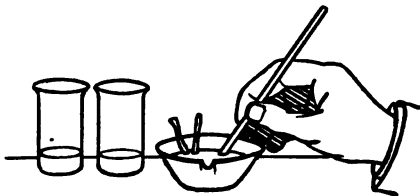
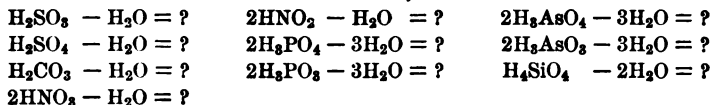
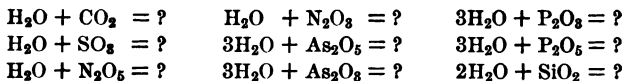


FIG. 52.

Exercises.—Write out these equations on paper—not in the book—completing the right-hand member.



131. Anhydrids.—Notice that the products, or right-hand members of the equations, are non-metallic oxids. *These products are called anhydrids, or acidic oxids, because each is formed by the breaking up of the corresponding acid into water and its non-metallic oxid, and the withdrawal of the water.* By combining water with a given anhydrid the corresponding acid is formed, as $\text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_3$. Complete the following, writing the full equation on paper.



Anhydrids are named like the acids to which they give rise. SO_2 is called sulfurous anhydrid because by the addition of water it forms sulfurous acid, H_2SO_3 . Affix the names to each of the anhydrids above.

BASES.

132. A Base is a substance which usually turns red litmus blue, and reacts easily with an acid, giving a salt and water; it is composed of a metal or positive radical, com-

bined with the OH radical. Bases are also called hydroxids or hydrates.

The three most common bases we shall discuss are sodium hydroxid, NaOH, potassium hydroxid, KOH, ammonium hydroxid, NH_4OH .

Exercises.—NaOH is the symbol of a base because it contains a metal united with OH. In the following list select the symbols of bases, and state why they are such: $\text{Ca}(\text{OH})_2$, HClO_2 , $\text{Mg}(\text{OH})_2$, NaNO_3 , HF, ZnCl_2 , $\text{Bi}(\text{OH})_3$, $\text{Zn}(\text{OH})_2$, HgI_2 , HCN, $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$.

133. Naming Bases.—If a metal has two valences, and hence two hydrates, the ending *ous* is applied to the one with the lower valence (or the one with less OH), and *ic* to the higher (or one with more OH); e.g., $\text{Fe}(\text{OH})_2$ is named ferrous hydrate, $\text{Fe}(\text{OH})_3$ ferric hydrate. This is in accord with the naming of acids (page 90). Name $\text{Cr}(\text{OH})_2$ and $\text{Cr}(\text{OH})_3$. Some metals do not form hydrates, as Ag, Au, Hg.

Complete, using pencil and paper, the symbols for bases with the following metals, and write the appropriate name after each.

Pb''	Fe'''	Cu''	Mn''	Sr''	Na'
Bi'''	Cr'''	Co''	Zn''	Ca''	K'
Cd''	Al'''	Ni''	Ba''	Mg''	NH_4'

134. Alkalis.—An alkali is a strong, caustic base which is very soluble in water. There are three common alkalis, KOH, NaOH, NH_4OH . The first two are often called fixed alkalis, the last the volatile alkali, since it readily breaks up into H_2O and the gas NH_3 .

Some other bases are soluble, but to a less extent, as $\text{Ca}(\text{OH})_2$. The carbonates of potassium, sodium, and ammonium, K_2CO_3 , Na_2CO_3 , $(\text{NH}_4)_2\text{CO}_3$, are known as alkalin carbonates, since they give an alkalin reaction.

135. Oxids.—These are of two kinds, acidic and basic. *An acidic oxid is the oxid of a non-metal which unites with water to form an acid, as CO_2 , SO_3 . $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$. A basic oxid is the oxid of a metal which unites with water to form a base, as Na_2O , CaO . $\text{Na}_2\text{O} +$*

$\text{H}_2\text{O} = 2\text{NaOH}$. Write the equations for the union of the following oxides with water to form bases: K_2O , CaO , BaO , MgO , ZnO , Fe_2O_3 . It will thus be seen that the oxide of a non-metal is the real root of an acid, and the oxide of a metal that of a base. Not all non-metallic oxides form acids, and some metallic oxides (with much oxygen), as CrO_3 , form acids. Acidic oxides and basic oxides unite to form salts.

Exp. 61. — (1) Pour into an evaporating dish 1 or 2 cc NH_4OH , add 4 or 5 cc H_2O , stir it, and taste a drop. If it has no taste add more NH_4OH . Dip the end of a piece of red litmus paper into it. (To redden blue litmus hold it in the fumes of HCl . To turn red litmus paper blue hold it in NH_3 fumes.) (2) Rinse the evaporating dish and test NaOH solution in the same way. Also (3) KOH solution. What do these experiments teach concerning bases?

SALTS.

136. A Salt is a substance which generally does not affect either blue or red litmus; it may be made by mixing an acid and a base, and in other ways; it is composed of a metal or a positive radical, united with a non-metal or a negative radical.

Sodium chlorid, or common salt, NaCl , is the one most often met with, but there exist others in great abundance and variety. All chlorides are salts of hydrochloric acid, all nitrates salts of nitric acid, sulfates of sulfuric acid, phosphates of phosphoric acid, etc. We know that KNO_3 is the symbol of a salt because it is composed of a metal, potassium, united with a negative radical, NO_3 .

Exercises. — In the following list select the acids, the bases, and the salts, remembering that acids begin with H and end with one or more non-metals; that bases begin with a metal and end in OH; and that salts begin with a metal and end in a non-metal: KBr , $\text{Fe}(\text{OH})_2$, HI , NaBr , HNO_2 , $\text{Al}(\text{OH})_3$, KClO_3 , HClO_3 , H_2S , K_2S , H_2SO_3 , K_2SO_4 , CaSO_4 , $\text{Ca}(\text{OH})_2$, CaCO_3 , NaBrO_3 , H_2CO_3 , HCN , K_2CO_3 , $\text{Cu}(\text{OH})_2$, $\text{Cu}(\text{NO}_3)_2$, PbSO_4 , H_3PO_4 , Na_3PO_4 .

137. Acid, Alkaline, and Neutral Reactions.— *An acid reaction is the turning of blue litmus red.* Practically all acids give this reaction. Some salts, especially acid salts, like HNaSO_4 , do the same. Acids as well as salts vary in the intensity of their action on litmus.

An alkaline reaction is the turning of red litmus blue. Bases give this reaction, especially the very strong and soluble ones called alkalis. Some normal salts also give this reaction, as Na_2CO_3 . HNaCO_3 when pure is neutral, but in drying it loses some CO_2 and contains a little Na_2CO_3 , hence it is alkaline. The last two may be explained as follows: Na_2CO_3 represents the very strong base NaOH and the very weak acid H_2CO_3 . So weak an acid has not the power to neutralize so strong a base, and although there is chemical union when the acid and base are put together, the product Na_2CO_3 is still alkaline.

A neutral reaction does not affect either blue or red litmus. It is no reaction at all, so far as concerns litmus. Many salts, especially normal ones, and all which can be made neutral by mixing an acid and a base, are neutral.

The explanation of these peculiar reactions of acids, alkalis, etc., on litmus is that there is a supposed litmus acid which is red, while its salts are blue. The salts are extremely sensitive to the action of any acid, and by that action litmus acid is formed, whereas when the action of bases overcomes the effect of the acid, the blue salt is formed. Most inactive salts are not strong enough to affect either the acid or the salts of litmus, and hence give neutral reaction.

Exp. 62.— (1) Pour into a clean evaporating dish 1 or 2^{cc} of NaCl solution, taste a drop of it, and test it with litmus, red and blue. Test in the same way (2) KNO_3 solution, also (3) a solution of $(\text{NH}_4)_2\text{SO}_4$. What is the usual action of salts on litmus? Test, however, these solutions with both colors: (4) Na_2CO_3 ; (5) CuSO_4 ; (6) HNaCO_3 ; (7) HNaSO_4 .

Test solutions of: (8) H_3PO_4 ; (9) $\text{H}_2\text{C}_2\text{O}_4$; (10) $\text{HC}_2\text{H}_3\text{O}_2$; (11) $\text{Ca}(\text{OH})_2$; (12) $\text{Ba}(\text{OH})_2$; (13) HNa_2PO_4 ; (14) $\text{Na}_2\text{B}_4\text{O}_7$; (15) NH_4NO_3 .

Exp. 63. — Put into a small beaker or a test tube 5^{cc} of an aqueous solution of blue litmus. (1) Pour a few drops of HCl into an evaporating dish, beaker, or test tube, and dip a stirring rod into this (never dip a rod into a reagent bottle), then stir the litmus solution with it, noting any change of color. If none occurs, add another drop of acid with the rod. (2) Pour a few drops of NH_4OH into a clean evaporating dish or test tube, dip the stirring rod into it, then stir the litmus solution with this. If the color is unchanged, repeat till blue is again obtained. (3) In the same way put a drop (or more, if necessary) of HNO_3 from an evaporating dish into the same blue solution. (4) When it is reddened add a drop or more of NaOH solution, until it becomes blue. (5) Change it again to red with a drop of H_2SO_4 , and (6) restore the color with KOH solution. (7) Add a few drops of H_2O to a solution of red litmus, and also to one of blue. (8) Add to both red and blue litmus solutions a solution of NaCl . (9) Try NH_4Cl solution. (10) KNO_3 solution. (11) HNaCO_3 solution. (12) HKSO_4 . (13) CuSO_4 .

138. Naming Acids and Salts. — A *binary* is a compound of two elements. A *ternary*¹ is a compound of three or more elements. The naming of binary compounds has been described (Chap. II). It remains to name ternary salts and acids, bases being called hydroxids or hydrates of metals. Ternary *acids* contain H and O, together usually with a non-metal. They are named from this last or characteristic element, the root of the word taking the ending *ic* or *ous* (as HNO_3 , nitric, and HNO_2 , nitrous), according to the quantity of O present, *ic* acids having the more. Now when the acid is made into a salt by replacing the H of the acid with a metal, the name of the metal is prefixed to the root of the second or non-metallic element, with the ending *ate* or *ite*, according to the proportion of oxygen it contains. KNO_3 is potassium

¹ The term *ternary* is not often employed at present, and only in distinction from *binaries*.

nitrate; KNO_2 potassium nitrite. The endings *ate* and *ite* always imply the presence of oxygen, the former more of it than the latter. An *ate* salt represents an *ic* acid; an *ite* salt an *ous* acid, *e.g.*, HNO_3 , KNO_3 ; HNO_2 , KNO_2 . Na_2SO_4 is sodium sulfate; Na_2SO_3 , sodium sulfite.

Exercises. — Name these: Na_3PO_3 and Na_3PO_4 ; CaSO_4 and CaSO_3 ; $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}_3(\text{PO}_3)_2$. CuCl_2 and CuCl are named, respectively, cupric and cuprous chlorids. Name: HgCl and HgCl_2 ; FeCl_3 and FeCl_2 ; NiCl_2 and NiCl_3 ; FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$; FeO and Fe_2O_3 ; $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$; HgI and HgI_2 ; $\text{Cr}(\text{OH})_2$ and $\text{Cr}(\text{OH})_3$; CoCl_2 and CoCl_3 ; Cu_2O and CuO . Acids are often named like salts, *e.g.*, HNO_3 is called hydrogen nitrate, and HNO_2 hydrogen nitrite. In fact an acid is sometimes defined as a salt of hydrogen. Name: H_2SO_4 , H_2SO_3 , H_3PO_4 , H_3PO_3 , H_2CO_3 , H_3AsO_3 , H_3AsO_4 .

If there are more than two acids in a series composed of the same elements, the prefixes *hypo* (less) and *per* (more) are used, *e.g.*, in the series HClO , HClO_2 , HClO_3 , HClO_4 ; HClO_3 is chloric acid; HClO_2 will then be chlorous, HClO hypochlorous, and HClO_4 perchloric. *Hypo* implies less of the negative constituent than *ous* alone, and *per* more of the negative than *ic* alone. The *ic* acid is usually the most common and important one, and must first be located in naming a series. Name: H_3PO_4 (*ic*), H_3PO_3 , H_3PO_2 ; HBrO (HBrO_2 does not exist), HBrO_3 (*ic*), HBrO_4 ; HIO_3 (*ic*), HIO_4 .

The prefixes *hypo* and *per* are employed in a similar way in naming salts; *e.g.*, NaClO , NaClO_2 , NaClO_3 , NaClO_4 are called, respectively, sodium hypochlorite, sodium chlorite, sodium chlorate, sodium perchlorate. Name: KClO , KClO_2 , KClO_3 , KClO_4 ; KBrO , KBrO_3 (*ate*), KBrO_4 ; KIO_3 (*ate*), KIO_4 ; $\text{Ca}_3(\text{PO}_2)_2$, $\text{Ca}_3(\text{PO}_3)_2$, $\text{Ca}_3(\text{PO}_4)_2$ (*ate*).

NORMAL, ACID, AND BASIC SALTS.

139. Basicity of Acids. — The H in an acid may be replaced by a metal, thus forming a salt. If sodium takes the place of hydrogen in HNO_3 , the compound becomes NaNO_3 . There is but one H atom in the molecule HNO_3 . In H_2SO_4 there are two H atoms; one or both of which

may be replaced with sodium, forming either HNaSO_4 or Na_2SO_4 . In H_3PO_4 there are three H atoms, and replacements as follows are possible with Na : H_2NaPO_4 (called primary sodium phosphate, from one atom of Na), HNa_2PO_4 (disodium, or secondary sodium phosphate), and Na_3PO_4 (trisodium, or tertiary sodium phosphate). Make the substitution with K' instead of Na ; with Ca''. Substitute Na for H in H_4SiO_4 . Different metals may also be substituted, *e.g.*, in H_3PO_4 we may have $\text{HNaNH}_4\text{PO}_4$ (hydrogen sodium ammonium phosphate).

The basicity of an acid is determined by the number of hydrogen atoms (replaceable by a metal) in its molecule. If it has one hydrogen atom, it is monobasic, as HCl ; if two atoms, bibasic, as H_2SO_4 ; if three, tribasic, as H_3PO_4 ; if four, tetrabasic, as H_4SiO_4 . In monobasic acids only one replacement is possible with a given metal, *e.g.*, HNO_3 , NaNO_3 . In bibasic acids two such replacements are possible, as in H_2SO_4 we may substitute sodium for half of the hydrogen or for all of it : HNaSO_4 or Na_2SO_4 . In tribasic acids three such substitutions are possible, etc.

140. Normal Salts. — *A normal salt is one in which all the hydrogen of the representative acid has been replaced with a metal.* KCl , Na_2SO_4 , $\text{Ca}_3(\text{PO}_4)_2$ are examples. Normal salts are not necessarily neutral to litmus, but may be acid or alkaline.

141. Acid Salts. — *An acid salt is one which contains hydrogen that can be replaced with a metal.* HNaSO_4 and HNa_2PO_4 are illustrations. It should be remembered that hydrogen is the acid element ; hence a salt containing it is called an acid salt. It may or may not give

an acid reaction. Hydrogen as part of a radical is not regarded as replaceable; *e.g.*, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ is a normal salt. If lead were dissolved in acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, only one-fourth of the hydrogen would be displaced by lead, hence the symbol of acetic acid is not $\text{H}_4\text{C}_2\text{O}_2$, but $\text{HC}_2\text{H}_3\text{O}_2$. The same is true of other metals acted on by acetic acid, and the acetate radical is $\text{C}_2\text{H}_3\text{O}_2$. Tartaric acid is $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, the tartrate radical being $\text{C}_4\text{H}_4\text{O}_6$.

142. Basic Salts. — *A basic salt is one which contains replaceable OH, or sometimes only O, from its representative base.* The OH of the base is replaceable with a non-metallic element or radical. If the base $\text{Bi}(\text{OH})_3$ should have its OH replaced in part by NO_3 , as $\text{Bi}(\text{OH})_2\text{NO}_3$, the product would be a basic salt, in this case called basic nitrate of bismuth. The basic salt BiOCl (bismuth oxy-chlorid, or bismuthyl chlorid) is made by pouring BiCl_3 into H_2O . $\text{BiCl}_3 + \text{H}_2\text{O} = \text{BiOCl} + \overbrace{2\text{HCl}}^{\text{acid}}$. Basic salts are not as a rule alkaline in reaction.

Exp. 64. — Into a test tube containing 10^{cc} of water pour a few drops of SbCl_3 , dissolved in HCl . Also add to water BiCl_3 solution in HCl .

143. Occurrence of Acids, Bases, Salts. — We have seen that acids and bases have very strong affinities, not only for each other, but also (especially the acids) for metallic elements and compounds. This is why they are not found, to any extent, on the earth's surface. A few springs and a South American river are known which contain free sulfuric acid, and sulfurous acid occurs in regions of active volcanoes. These flowing over other substances combine with them and form salts. A trace of nitric acid is found in the air. Salts, on the other hand, are extremely abundant in nature. Most rocks are very complex silicates. Carbonates, sulfides, and sulfates, which are salts of their respective acids, form the ores of a large number of metals, and are found very widely diffused.

CHAPTER XIII.

PREPARATION OF SALTS, ACIDS, AND BASES.

SALTS.

144. Having studied the characteristic properties of acids, bases, and salts, their notation and nomenclature, it is of the highest importance that the student should know how these classes of products may be prepared in the laboratory. Fortunately a few simple principles govern the preparation. We begin with salts, all of which may be divided into two classes, dependent upon whether or not they are dissolved by water.

145. Soluble and Insoluble Substances. — *All the common acids mentioned in this book are soluble. Bases and salts are either soluble or insoluble. A soluble substance is one which dissolves quite freely in water.* Common salt and sugar are examples. *An insoluble substance is one which does not dissolve, or dissolves very slightly, in water.* Silica, SiO_2 , and lead sulfate, PbSO_4 , are examples. Perhaps no substance is wholly insoluble, and there are all grades of solubility from the very soluble to the very insoluble. BaSO_4 is one of the most insoluble; but one part of it will dissolve in some 800,000 parts of water, whereas MgSO_4 dissolves in some 3 parts of water. It is thought that all existing elements are in solution in the ocean. If a solid needs, say, 1000 parts of water to dis-

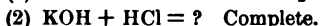
solve it, it is said to be insoluble or very slightly soluble. There are many other solvents besides water, such as alcohol, ether, carbon disulfid, and the various alkalis and acids, but unless special mention is made of these, water is the solvent referred to. We must distinguish clearly between soluble and insoluble substances, for this forms the basis of chemical analysis, and the two classes are made in different ways.

146. (1) Neutralization. — *One method of preparing soluble salts is by neutralization.* On making a mixture of an acid and a base (in solution) a reaction takes place, and a salt is formed. As a salt usually gives a neutral reaction, a point is reached in the mixing, if it is done very carefully, at which the whole mixture is neutral to pieces of red and blue litmus paper. The process is called *neutralization*. If the solvent water is evaporated at this point, the salt is obtained as a solid.

Exercises. — Neutralizing each of the three alkalis with hydrochloric acid, we obtain three different salts:



FIG. 53.



Notice that the plus part of the base combines with the minus of the acid, and the hydrogen of the acid with the OH of the base to form water, which is always a product of neutralization. By using nitric acid with the above alkalis we could obtain other salts, and with sulfuric acid still others. Write equations for each, and name the salts, stating how you would prepare them. How would you make KI from its acid and base? Write the equation. How KBr? NaBr? Some salts are not neutral, hence the acid cannot be neutralized by the base, or *vice versa*.

Exp. 65. — Pour into an evaporating dish not over 5^{cc} NaOH solution, and into a clean test tube or beaker 4 or 5^{cc} HCl. Now add some of this

latter, a little at a time (Fig. 53), to the NaOH solution, stirring it meantime till the product is neutral to litmus paper; when nearly neutral add a drop at a time with a stirring rod, and test with both colors, using only the end of the paper and keeping it on the side of the evaporating dish (Fig. 54). If blue litmus paper is reddened by the solution, add NaOH solution, a few drops at a time.

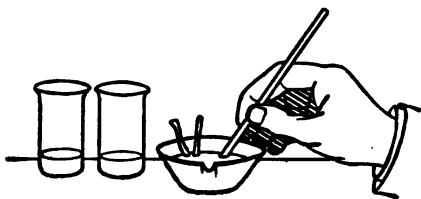


FIG. 54.

If red litmus is turned blue, add a drop of HCl. When the solution does not affect either red or blue litmus, left in it for a minute, show it with both papers in it to the instructor, then filter and evaporate the liquid to dryness by boiling it over a plate and asbestos paper (Fig. 55). When it is cool, examine the residue and taste it.

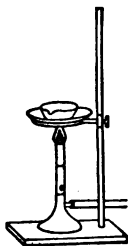


FIG. 55.

Exp. 66. — Into an evaporating dish put 5cc KOH solution, and neutralize it with dilute H_2SO_4 , using both test papers. When sure it is neutral, evaporate most of the water and taste the product. Neutralize NH_4OH with HNO_3 (preferably dilute) in the same way as before. Stop evaporation when dense fumes begin to appear. These fumes indicate a decomposition of the salt by heat.

147. (2) Acid and Metal. — *Soluble salts may also often be made by dissolving a metal in an acid.* It is called a chemical solution, and consists of two stages: (1) the metal combines with the negative part of the acid, thus forming a salt; (2) the salt is dissolved in the liquid, most of which is water. We see from this why a salt which is insoluble in water is not usually made in this way. Some soluble salts cannot be made in this way, for the metal will not react with the given acid, *e.g.*, Ag and $\text{HC}_2\text{H}_3\text{O}_2$.

148. Application. — It will be recalled that zinc chlorid, ZnCl_2 , was made by the above principle, also silver nitrate, AgNO_3 , copper nitrate, $\text{Cu}(\text{NO}_3)_2$, etc. By reference to Table A (Appendix) it is seen

that silver chlorid is an insoluble salt, and hence HCl will not act on silver, but nitric acid will dissolve it, because AgNO_3 is soluble. Would HCl be likely to act on Pb? Would acetic acid probably react with Pb, and dissolve it? Write half a dozen equations for salts made in this way. Owing to the exceptions stated above, this rule is not infallible.

Exp. 67. — To a piece of zinc in a test tube add water and HCl. When the action stops, pour the liquid into an evaporating dish, and evaporate to dryness. Try to dissolve the residue in H_2O .

Exp. 68. — Dissolve a few bits of iron filings in dilute H_2SO_4 , then add water, filter, and evaporate the filtrate. Try to dissolve the residue.

Exp. 69. — Dissolve a little copper in dilute HNO_3 , then filter and evaporate as before; finally add H_2O .

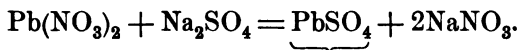
149. (3) Acid and Salt. — *Soluble salts may be made by acting on other salts or compounds with an acid.* Metallic oxids, carbonates, and sulfids are the most common of these. Suppose we wish to make some calcium chlorid, CaCl_2 . We find from the table that it is soluble, and infer that HCl will probably dissolve calcium. But we also learn that the metal calcium sells at ten dollars a gram, and cannot be had in the laboratory, so we next look for an inexpensive compound upon which HCl will act. The carbonate, CaCO_3 (limestone or marble), is abundant, and HCl attacks it vigorously.

150. Application. — In cases where the metal is cheap and easily obtained, the acid is used to act directly upon that; in other cases some salt is taken, the carbonate being a usual one, but an oxid, chlorid, sulfid, etc., may often be used with different acids. If the chlorid is wanted, HCl is the acid employed; if the nitrate, HNO_3 ; if the sulfate, H_2SO_4 ; if the acetate, $\text{HC}_2\text{H}_3\text{O}_2$. Heat may or may not have to be applied. To obtain the salt as a solid, the water or other liquid must be evaporated. The following are typical reactions: (1) $\text{CaCO}_3 + 2\text{HCl} = \text{CaCl}_2 + \text{H}_2\text{O} + \widetilde{\text{CO}_2}$; (2) $3\text{CuS} + 8\text{HNO}_3 = 3\text{Cu}(\text{NO}_3)_2 + 4\text{H}_2\text{O} + 3\text{S} + \widetilde{2\text{NO}}$.

Exp. 70. — To a piece of marble, CaCO_3 , in a test tube, add H_2O and HCl . When the action stops, evaporate the liquid, and see whether the residue will dissolve in water.

Exp. 71. — Add some dilute HNO_3 to 2g of PbO (litharge) in an evaporating dish and heat it for some time, then decant on a filter. Evaporate the filtrate and add H_2O .

151. Insoluble Salts. — *An insoluble salt may be made by mixing two solutions, one of which contains a compound of the metal, the other a compound of the non-metallic part of the insoluble salt, which will appear in the mixture as a precipitate.* Lead sulfate, PbSO_4 , is made by pouring a solution of lead nitrate, $\text{Pb}(\text{NO}_3)_2$, upon one of sodium sulfate, Na_2SO_4 .



Any other soluble lead salt and any other soluble sulfate would have done equally well.

Exercises. — Would a mixture of lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, and KCl (both in solution) be likely to form PbCl_2 ? $\text{Pb}(\text{NO}_3)_2$ and NH_4Cl ? What salts of lead are soluble (Table A)? How would you prepare PbS ? PbI_2 ? BaSO_4 ? $\text{Ba}_3(\text{PO}_4)_2$? HgCl_2 ? CuI_2 ? CuS ? Write equation for the above.

152. Union of Elements. — *Many salts, both soluble and insoluble, can be made by the direct union of their elements.* Copper sulfid, CuS , and ferrous sulfid, FeS (Chap. II), are examples. NaCl can be made by passing chlorine over sodium. In many cases a high temperature is required for chemical union, in others the element should be in the nascent state, in still others only ordinary conditions are necessary.

Exp. 72. — Add the following solutions to some lead nitrate solution in separate test tubes: (1) KI ; (2) KBr ; (3) NaCl ; (4) HgCl_2 ; (5) K_2CrO_4 ; (6) H_2SO_4 . Try each of the above with lead acetate solution.

ACIDS.

153. *Acids are usually made by acting with sulfuric acid on a salt of the acid required.* We have seen that salts can be made by the union of an acid and a base, and we now learn that an acid can be obtained from its representative salt. Sulfuric acid is taken for making acids, because it readily parts with its hydrogen and takes a metal in its place. For that reason, H_2SO_4 is sometimes said to be the strongest of acids, but this is true only in the sense named above. A salt of the acid desired must be put with the H_2SO_4 ; *e.g.*, if HCl is wanted, NaCl or some chlorid must be used; if HNO_3 , some nitrate, as KNO_3 , should be employed; if $\text{HC}_2\text{H}_3\text{O}_2$, some acetate, as $\text{NaC}_2\text{H}_3\text{O}_2$.

Exercises. — State how hydrogen sulfid, H_2S , might be made. How oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$. Hydrocyanic acid, HCN . Tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$. Sometimes other acids than H_2SO_4 can be used, as HCl , in making H_2S or H_4SiO_4 . Nitric acid breaks up too easily, giving rise to oxids of nitrogen. Hence it is not employed to make other acids. Sulfuric acid is not made by the above process, but is built up from its elements.

BASES.

154. **Bases**, or metallic hydroxids, are either soluble or insoluble. The alkalis and those of the alkaline earth metals are soluble, the rest are not.

Soluble bases may be made by acting with calcium hydroxid on certain salts of the base required. Other bases, *e.g.*, sodium or potassium hydroxid, may be used in place of $\text{Ca}(\text{OH})_2$. NH_4OH is prepared from a salt of ammonium, as NH_4Cl , NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, etc., by heating

it with a mixture of calcium hydroxid (slaked lime). $2\text{NH}_4\text{Cl} + \text{Ca}(\text{OH})_2 = \text{CaCl}_2 + 2\text{NH}_4\text{OH}$. Sodium hydroxid, NaOH , is made from sodium carbonate, Na_2CO_3 , and calcium hydroxid. NaCl cannot be used, as it does not break up by the action of lime. KOH is made in a similar way from K_2CO_3 .

Insoluble bases are made by mixing two solutions, one of which contains a base and the other a compound of the metal of the base required. $\text{Fe}(\text{OH})_3$ can be obtained by adding NaOH solution to one of FeCl_3 . Any other soluble ferric salt would do as well, and any other soluble hydroxid.

Exercises. — Write equations for making NaOH , KOH , $\text{Fe}(\text{OH})_3$, $\text{Bi}(\text{OH})_3$. Calcium hydrate itself is not made in this way, but is synthesized from CaO and H_2O .

Exp. 73. — Add NH_4OH to solutions of AlCl_3 , FeCl_3 , CrCl_3 . Try the same solutions with NaOH solution.

The preparation of the alkalis is given specially in the following chapters. The accompanying table should be carefully studied.

TABLE ILLUSTRATING PREPARATION OF ACIDS, BASES, SALTS.

ACIDS.

Types:	HCl	HF	HNO_3	H_2S
Made from H_2SO_4 and	NaCl	CaF_2	NaNO_3	FeS
Exceptions:	HBr	HI	H_2SO_4	Aqua regia
Made from	Br , P , H_2O	I , P , H_2O	SO_2 , NO , O , H_2O	HCl , HNO_3

BASES.

Types:	NH_4OH	KOH	NaOH	$\text{Fe}(\text{OH})_3$
Made from $\text{Ca}(\text{OH})_2$ and	NH_4Cl	K_2CO_3	Na_2CO_3	FeCl_3
Exceptions:	$\text{Ca}(\text{OH})_2$			
Made from	CaO , H_2O			

SOLUBLE SALTS.

Types:	ZnCl_2	$\text{Cu}(\text{NO}_3)_2$	FeSO_4	HgCl_2
Made from	Zn, HCl	Cu, HNO_3	$\text{Fe, H}_2\text{SO}_4$	Hg, aqua regia

or from oxids, hydroxids, carbonates, etc., of the metal and the respective acids.

INSOLUBLE SALTS.

Types:	PbCl_2	PbSO_4	PbS	PbCrO_4
Made from $\text{Pb}(\text{NO}_3)_2$ and	HCl	H_2SO_4	H_2S	K_2CrO_4

or from mixtures of soluble salts, one containing the positive part, the other the negative part, of the insoluble salt.

155. Saturated Solution. — Water dissolves many solids, liquids, and gases. Solids and gases that dissolve are said to be soluble; liquids that dissolve or mix are said to be *miscible*, as alcohol is miscible in water. Some solids and gases are far more soluble than others; MgSO_4 will dissolve in 3 parts of water, CaSO_4 in 400 parts. Oxygen is but slightly soluble, whereas some 500 volumes of HCl dissolve in one volume of water. Solubility varies also with temperature. As a rule—to which there are some exceptions—hot water will dissolve more of a given solid than cold water. The reverse is true of gases. PbCl_2 is quite soluble in boiling water, but very slightly so in cold.

We shall here discuss only solids. When a solvent holds in solution all of a given solid or gas that it can retain, it is said to be *saturated*. Heating it further increases its capacity for solids, cooling it diminishes that capacity. If water heated to 90° is saturated with a given solid, and is then cooled to, say, 50° , the excess of solid is thrown out of solution, or precipitated. Water is

the most common solvent, but the principle above stated applies to others.

156. Supersaturated Solution. — When water is saturated, or nearly so, with a given salt, at one temperature, and is then cooled slowly and quietly, the cooled liquid may hold in solution more of the solid than would suffice to saturate it at that temperature. It is then said to be *supersaturated*. Agitation and especially the introduction of a little solid matter in such a solution starts precipitation, which continues until the liquid is only saturated.

157. Crystallization. — When a saturated liquid is cooled and the solid precipitates, the latter is quite likely to form in crystals, especially if the cooling be slow. Evaporating the liquid from a saturated solution precipitates the solid, often in crystalline form. These are crystals from solution. They may also be obtained from *fusion*, i.e., melting a crystalline substance and allowing it to cool slowly. A fourth way to obtain crystals is to make an insoluble compound in the usual way, by mixing two solutions. Generally precipitates obtained in this way are *amorphous* or indistinctly crystalline, as time is not given for the forces of crystallization to arrange the molecules in crystalline form. Crystals may also be obtained by sublimation from a vapor. Some substances do not crystallize at all, and are called *amorphous*.

158. Systems. — All varieties of crystals — of which there are hundreds — are divided into six classes or systems: (1) the *isometric* system (of which the cube is a type), whose 3 axes (Fig. 56) are at right angles, and of equal length; (2) the *tetragonal* system, in which the axes are all at right angles, but one is shorter or longer than the others (Fig. 57);

(3) the *orthorhombic* system, in which the axes are at right angles, but all differ in length (Fig. 58); (4) the *monoclinic* system, in which only two axes are at right angles to each other, and all are of different lengths (Fig. 59); (5) the *triclinic* system, in which all axes are of different lengths and none at right angles (Fig. 60); (6) the *hexagonal* system, in which there are four axes, three being equal in length, and at 60° from each other, the fourth unequal and at right angles to the others (Fig. 61). The action of polarized light on the section of a crystal is useful in determining to which system it belongs.

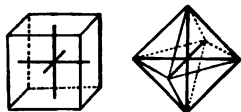


FIG. 56.

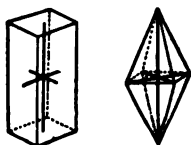


FIG. 57.

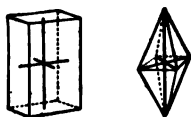


FIG. 58.

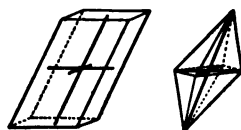


FIG. 59.

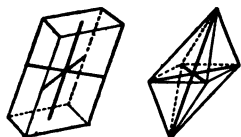


FIG. 60.

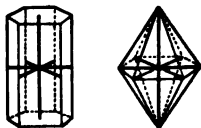


FIG. 61.

159. Water of Crystallization. — Many substances precipitating from solution take up water in crystallizing. Such water is called *water of crystallization*. Sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$; alum, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, are examples. Symbols of such molecules are written as above. The water can usually be expelled by heat. Sometimes all the water but one molecule can be expelled at, *e.g.*, 100° , but the last molecule may require a much higher temperature.

160. Efflorescence and Deliquescence. — Very often if salts containing water of crystallization are exposed to the air, the water or part of it evaporates. Such a salt is *efflorescent*. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is an efflorescent salt. When such crystals lose their water of crystallization they fall to a powder, and — if they were colored — lose the color and become white.

Some substances, which do not take up water of crystallization, still have great affinity for water, so much so that they absorb it from the air, and literally dissolve themselves, thus becoming liquids. These salts are called *deliquescent*.

Exp. 74. — Fill an evaporating dish two-thirds full of water, heat it,

and add small pieces of alum until the liquid becomes thick. Now put in a narrow piece of cotton cloth so that it lies in the liquid but does not touch the bottom of the dish, and set the latter aside to cool.

Exp. 75. — Cautiously boil about 5s copper sulfate in 5cc H_2O in a test tube until it is dissolved. Then place the test tube in an oblique position and let the liquid cool. If necessary, leave it till the next laboratory hour. Note the formation of crystals, and observe their form, color, lustre, angles, etc.

Exp. 76. — Dissolve Glauber's salt, $Na_2SO_4 \cdot 10H_2O$, to saturation in water at 33° , then let the liquid cool. If no crystals form after some time, add a small crystal of the salt.

Exp. 77. — Melt 15 or 20s of sulfur in a small Hessian crucible (covered to prevent combustion), then cool it, and as it begins to solidify on the surface pour most of it into water, and watch the remainder, breaking the crucible when it is cold.

Exp. 78. — Put into an evaporating dish as much powdered sulfur as will stay on the point of a small knife blade, and cover it with a very little carbon disulfid, CS_2 , so as to dissolve it. Place the dish in a draft of air and watch the result as the CS_2 evaporates. Put a drop of the solution on a microscopic slide, and observe the formation of crystals under the microscope.

Exp. 79. — Drop into a test tube or flask one or two crystals of iodine, and heat them a moment. Presently examine the sides of the tube or flask.

Exp. 80. — Put a crystal of ferrous sulfate and a small piece of calcium chlorid on separate pieces of paper, and leave them in the locker exposed to the air for several days.

CHAPTER XIV.

HYDROCHLORIC AND HYDROFLUORIC ACIDS.

HYDROCHLORIC ACID.

161. In the first part of the nineteenth century, when sodium carbonate began to be made in large quantities in England, the hydrochloric acid gas — which was a by-product — was allowed to escape into the air. It killed all vegetation and vitiated the air, so that laws were passed which compelled the manufacturers to get rid of the gas. The only way to do this was to save it. A spray of water was made to fall through the towers, thus dissolving the ascending gas. Soon uses were found for the acid, which is now one of the indispensables of civilized life.

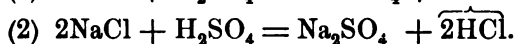
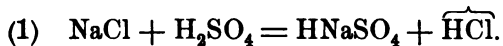
162. History. — Basil Valentine, in the fifteenth century, first described the preparation of this acid by a process similar to the one we now use. He called it "spirit of salt." Priestley, in 1772, first collected it over mercury (calling it *marine acid air*), and Davy in 1810 proved its composition to be hydrogen and chlorine.

163. Names. — Hydrogen chlorid, hydric chlorid, hydrochloric acid, chlorhydric acid, muriatic acid, spirit of salt.

164. Occurrence. — The free occurrence of hydrochloric acid in nature is rare, as its affinities are too strong. It is one of the gases evolved during eruptions of Vesuvius and other volcanoes, and it exists in waters of some rivers which have their origin in volcanic mountains. It forms a part of the digestive fluids of the stomach. Its

most abundant salt is sodium chlorid, but other chlorids are common and widely diffused.

165. Preparation. — The usual mode of preparing the acid, either in the laboratory or on a large scale, is to treat sodium chlorid, NaCl , with sulfuric acid, H_2SO_4 . It is better to mix a very little water with the acid. Chemical action begins at once even in the cold, as shown by the effervescence and the suffocating fumes which rise. This action is increased by the application of heat. Either of two reactions may take place.



Moderate temperature gives (1), a red heat (2). It should be noted that in (1) the acid salt HNaSO_4 , primary sodium sulfate, is formed, and in (2) the normal or secondary sulfate Na_2SO_4 , also that in (2) there is an economy in the use of H_2SO_4 , as regards the HCl produced, whereas a higher temperature is needed — a gain in the one case, and a loss in the other. Other chlorids might be used, but NaCl is least expensive. The preparation of HCl on a large scale occurs in the sodium sulfate manufacture, which is carried on mainly in England.

Hydrogen chlorid is also formed by the direct union of its elements. In strong sunlight the two mixed elements combine with explosive violence. Hydrogen and chlorin have intense affinity for each other, and either will burn in an atmosphere of the other, giving HCl . In fact, the acid is formed in almost every case where chlorin comes in contact with compounds of hydrogen. One volume of hydrogen invariably unites with one volume of chlorin and forms two volumes of hydrogen chlorid; or one part by weight of hydrogen attaches itself to thirty-five parts by weight of chlorin.

Exp. 81. — Fill two receivers one-fourth full of water, and connect them with a flask, as in Fig. 62. The receiver with the 3-holed cork is called a

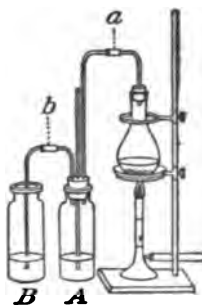


FIG. 62.

Wolff bottle. A series of three such bottles is shown in Fig. 63. Put into the flask 10 or 15 $\frac{1}{2}$ NaCl and add 20 $\frac{1}{2}$ H_2SO_4 , previously mixed with 5 $\frac{1}{2}$ H_2O and cooled. Heat the mixture 10 or 15 minutes over asbestos, but do not let the frothing extend to the neck of the flask. Look closely in the Wolff bottle for any action. Finally disconnect the apparatus at *a* and pass some of the gas over a few drops of NH_4OH in an evaporating dish. Pass some of the gas into a solution of blue litmus. Thrust a burning splint into the flask. Avoid inhaling the gas. The antidote is NH_3 inhaled from a handkerchief.

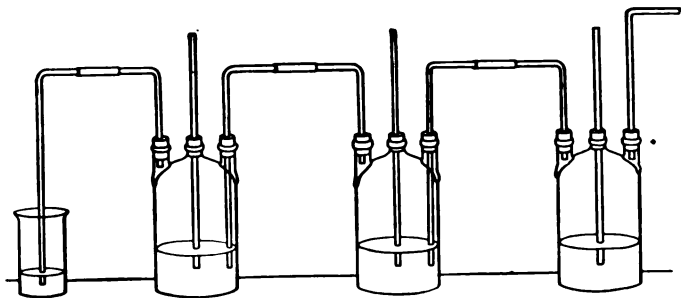


FIG. 63.

166. Properties. — *Physical.* Hydrogen chlorid is a colorless gas, sour, irritating, irrespirable, poisonous, and a little heavier than air. It has an acid reaction, and is very soluble in water, one volume of which at 0° will dissolve some 500 volumes of the gas with liberation of heat. The solution then contains 43% of HCl. The commercial acid (called muriatic) contains about one-third acid and two-thirds water. The yellow color is due to iron salts

or organic matter, besides which it contains compounds of sulfur and sometimes arsenic, which are derived from the impure H_2SO_4 and NaCl . The C. P. (chemically pure) acid is without color. This may be distilled at 110° , when it gives a liquid containing 20% HCl , and corresponds to the symbol $\text{HCl} + 8\text{H}_2\text{O}$. If the liquid contains more HCl , heat liberates the gas; if less, heat liberates H_2O . The gas can be liquefied at -102° and solidified at -116° . HCl , on escaping into the air, forms a white cloud with the moisture. A temperature of 1800° is necessary to dissociate HCl gas.

Chemical. HCl will not support ordinary combustion, but K and Na burn vigorously in it after being first set on fire, KCl and NaCl being formed and hydrogen liberated. The acid dissolves most metals, forming with them chlorids and hydrogen. Ag , Pb , Hg , Cu , Au , Pt are either not at all or but slightly dissolved by it. AgCl , PbCl_2 , HgCl are insoluble, and while the higher chlorids of the other three are soluble, the affinity of H for Cl is stronger than that of Cl for the metals. Free Cl (as in aqua regia or euchlorin) dissolves the metals Cu , Au , Pt , and Hg and forms their chlorids. Soluble chlorids are made by dissolving in HCl either the metal or some of its salts which are transposed by it. Insoluble chlorids may be made by adding HCl to solutions of the soluble salts of those metals, *e.g.*, $\text{Pb}(\text{NO}_3)_2$, AgNO_3 , HgNO_3 . If we should take solutions of the soluble salts of all the common metals (Table A, Appendix), *e.g.*, the nitrates, each in a separate test tube or beaker, and add HCl to them, only the three above named would give a precipitate. This is but another way of saying that there are only three insoluble chlorids, PbCl_2 , AgCl , HgCl .

167. Separations. — Suppose now we were to mix solutions of $\text{Pb}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$, the lead could be separated from the copper by HCl , for the former would precipitate and the latter remain in solution. On filtering, the lead would remain on the filter as a residue, PbCl_2 , and the copper would pass into the filtrate unchanged as $\text{Cu}(\text{NO}_3)_2$ and could be precipitated by H_2S as PbS . A mixture of Pb , Ag , and Hg salts could, by the same reagent, be separated from other salts in solution. This is exactly what is done in analysis.

168. Tests. — The following tests may be applied to a substance supposed to contain HCl . If the latter is present, these results will appear: (1) A suffocating odor peculiar to itself. (2) Bluish white fumes of NH_4Cl , when HCl is in contact with ammonia. (3) The gas will not support combustion nor burn. (4) Hydrogen is liberated and may be burned when HCl solution is brought in contact with zinc. (5) It gives a white precipitate with either of these solutions: (a) $\text{Pb}(\text{NO}_3)_2$, (b) AgNO_3 , (c) HgNO_3 . Any soluble chlorid will give (5). The result obtained in (a) dissolves in boiling water, (b) in NH_4OH , (c) in aqua regia. N , CO_2 , etc., act in the same way as (3), H_2SO_4 gives a result like (4), other gases give the same colored fumes as (2), and other odors may be mistaken for HCl . Hence all the above tests should be applied, together with the litmus test.

Exp. 82. — (1) Test the liquid in each bottle (Exp. 81) with blue litmus paper. (2) Taste a drop from the stirring rod. (3) Cautiously note the odor. (4) Put a piece of zinc into a test tube and pour over it 5 or 10^{cc} of the contents of the first bottle.

Exp. 83. — Pour into separate tubes 5^{cc} of each of these solutions and then pour over each a little of the acid in the first bottle. (1) $\text{Pb}(\text{NO}_3)_2$, (2) AgNO_3 , (3) HgNO_3 , (4) $\text{Hg}(\text{NO}_3)_2$, (5) FeCl_3 , (6) CuCl_2 .

Exp. 84. — Mix solutions of $\text{Pb}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$, 10^{cc} in a test tube, add HCl and filter. Which metal is on the filter? Add H_2S solution to the filtrate.

169. Uses. — The main use of this acid is for making chlorids, both soluble and insoluble, also in preparing other

compounds of chlorin and the element itself. In the laboratory it is employed for generating hydrogen, also in analysis, and in making aqua regia. It furnishes chlorin, from which bleaching powder is made. The silver chlorid, AgCl , in photography is deposited upon the photographic paper from solutions of AgNO_3 and NaCl .

$$\text{AgNO}_3 + \text{NaCl} = \underbrace{\text{AgCl}} + \text{NaNO}_3.$$

HYDROFLUORIC ACID.

170. Hydrofluoric Acid, HF, is prepared from powdered *fluorite*, CaF_2 —the only common fluorid which is native—by action of H_2SO_4 in leaden vessels. $\text{CaF}_2 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + 2\text{HF}$. It is an intensely corrosive gas, very soluble in water, attacking most metals. Au, Pt, Pb, etc., are not much affected by it. It especially reacts vigorously with silica, SiO_2 , and hence is used to mark or etch glassware. This prevents the solution from being kept in glass bottles, which it would gradually dissolve. It is kept in either gutta percha or lead bottles. The marking is done either by the gas, as it is made, or by the solution applied with a camel's hair brush. The article to be etched is first covered with a thin layer of paraffin, through which the design is traced with a sharp point, thus exposing the glass, which the fumes or liquid come in contact with and attack. $4\text{HF} + \text{SiO}_2 = 2\text{H}_2\text{O} + \text{SiF}_4$.

Exp. 85.—Clean a piece of glass with alcohol, cover it thinly on one side with paraffin, warming the other side to have it spread evenly. Trace any lettering or design (Fig. 64) through the paraffin, with a pointed object, *e.g.*, a file handle. Pour a little HF into a leaden dish—be very careful not to get any on the flesh—and with a camel's hair brush cover the marked parts several times with the solution and leave for a few minutes. The wax can be melted and scraped off and the glass washed in alcohol or naphtha. A graduate may thus be made from a test tube. The glass may be etched by HF fumes by mixing CaF_2 with a little H_2SO_4 in a leaden dish, and laying the exposed side of the glass over it for several hours.



FIG. 64.

CHAPTER XV.

NITRIC ACID AND AQUA REGIA.

NITRIC ACID.

171. By far the most important compounds of nitrogen in commerce are nitrates. These are either formed by nature, or are artificially prepared from nitric acid, or from a vegetable ferment, and they have a very important bearing on the arts of civilization, in furnishing material for the growth of food plants, in the manufacture of explosives, and in the making of such products as sulfuric acid and celluloid. Nitrates are great oxidizing agents, and on this account the properties of nitric acid are of special interest.

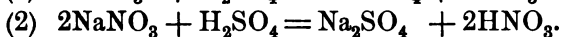
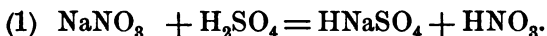
172. History.—Nitric acid was known by Geber probably in the eighth century, but not till 1784 was its exact composition made known by Cavendish, who showed that it could be made by combining N, O, and H_2O by an electric spark.

Names.—Hydrogen nitrate, hydric nitrate, nitric acid, aqua fortis, spirit of nitre.

173. Occurrence.—The acid itself has too strong affinities to exist in any quantity in nature. A trace of it is found in the air, especially after electric discharges. Two nitrates, $NaNO_3$ and KNO_3 , are, however, found in quite large quantities, especially the former, which is obtained mostly from Chile, and is known as Chile saltpetre. KNO_3 , called *nitre* or *saltpetre*, is found

in India and other warm Eastern countries. Both nitrates are the products of certain species of micro-organisms, feeding upon decaying organic matter. Sweden has nitre plantations where NaNO_3 is made by introducing the proper germ into such matter, allowing the latter to ferment, and then dissolving the product in water, and crystallizing by evaporation.

174. Preparation. — The acid is made both on a large scale and in the laboratory by the action of sulfuric acid on some nitrate, generally NaNO_3 or KNO_3 . The former is more abundant and cheaper than the latter. Other nitrates are mostly artificial products made from HNO_3 , and are not well adapted for making the acid, as they are more expensive.



It will be seen that the above equations are similar to those in the making of HCl , in that a moderate heat gives an acid salt, and a higher temperature the normal salt. In the laboratory experiments moderate heat should be applied. Even at 86° some of the acid breaks up into NO_2 , H_2O , and O . $2\text{HNO}_3 = \text{H}_2\text{O} + 2\widetilde{\text{NO}_2} + \widetilde{\text{O}}$. Red fumes, NO_2 , show this dissociation, and these dissolved in the acid impart a yellow or red color and increase its strength. It is then called *fuming nitric acid* and is extremely powerful and corrosive. After a time the fumes will mostly evaporate, though some combine with any H_2O and O present and form HNO_3 . Sunlight breaks up the strong commercial acid, as may be seen by letting a bottle of it stand in the direct rays of the sun.

175. Manufacture. — On the large scale HNO_3 is usually made at sulfuric acid works, the apparatus being (Fig. 65) iron retorts, *B*, and earthen condensers, *C*. The acid is afterwards distilled. If it is weak, H_2O distils over first; if strong, HNO_3 goes over first, but an acid of

constant composition (specific gravity 1.4) is finally obtained containing 68% HNO_3 , which is the commercial variety.

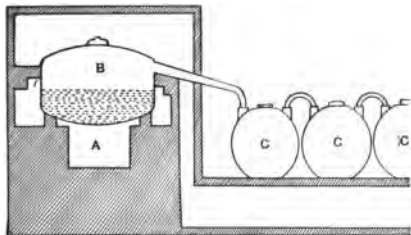


FIG. 65.

Exp. 86.—Introduce into a glass retort through the tubulure 10 or 15^g of fine NaNO_3 and 25 or 30^{cc} H_2SO_4 . Adjust the apparatus as in Fig. 66, having the neck of the retort pass

to the bottom of a large test tube, which is surrounded by water in a wide tumbler or bottle. The water is to cool and condense the acid from the vaporous state in which it passes over. Apply the Bunsen flame for 15 or 20 minutes. Notice the liquid running down the neck of the retort, and the fumes, also the color of the liquid obtained. Na_2SO_4 is left in the retort. This may be blackened by carbon. Use great care not to get any acid on the hands. The antidote, after thorough washing, is HNaCO_3 .

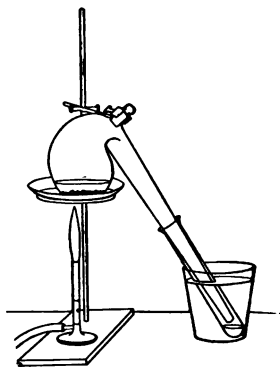


FIG. 66.

176. Made from Elements.—Minute quantities of the acid may be made by passing an electric spark through a mixture of the three gases, H , N , O , in a tube over mercury (Fig. 67). State what

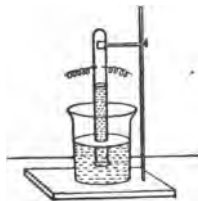


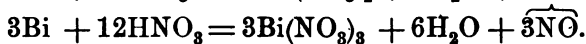
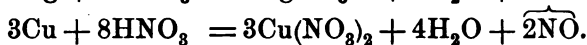
FIG. 67.

the right proportion—by volume and also by weight—would be. An electric discharge causes the hydrogen and part of the oxygen to combine to form H_2O , and the nitrogen to combine with more oxygen and form NO_2 . These two products unite to form HNO_3 . $3\widetilde{\text{NO}}_2 + \text{H}_2\text{O} = 2\text{HNO}_3 + \widetilde{\text{NO}}$. The same thing is done with a mixture of air and oxygen over sodium hydroxid to dispose of the nitrogen and leave argon. The acid formed unites with the base NaOH , and thus all combinable products

are obtained in solution and argon is left. Trace out each step, with equations. Electric discharges in the air during thunder storms are supposed to produce nitric acid in the same way.

177. Properties. — *Physical.* HNO_3 is a very corrosive, poisonous, pungent liquid, with a sour taste and acid reaction. It is miscible in water in all proportions, the commercial acid being about one-third water. It boils at 86° and freezes when pure at -47° .

Chemical. There are few elements, even non-metals, which do not react with it, and it changes most compounds. With four exceptions it dissolves all common metals, forming with them nitrates, and usually water and an oxid of nitrogen (more often nitric oxid, NO). The typical reactions are:



Sometimes other reactions take place, giving NO_2 , N_2O_3 , N_2O , N , or even NH_3 . The reaction depends upon three things: (1) the strength of the acid used; (2) the temperature applied to the mixture; (3) the metal used.

178. Explanation of Reactions. — The beginner usually writes the equation, following the analogy of HCl or H_2SO_4 on zinc, as follows: $\text{Zn} + 2\text{HNO}_3 = \text{Zn}(\text{NO}_3)_2 + \widehat{2\text{H}}$. Why does not this reaction take place? Probably it may momentarily at first; but HNO_3 is very easily broken up, and it contains hydrogen, a reducing agent, and oxygen, an oxidizing agent. When the molecules of the acid have been broken up by the metal, both these elements are in the nascent state, and hence they combine, all the hydrogen seizing enough oxygen to form water, leaving the rest to make a nitrate of the metal and the oxid of nitrogen. The equations should be carefully studied as an illustration of the action of a reducing agent in connection with an oxidizing agent.

Hence the reaction above is superseded by this: $\widehat{3H} + HNO_3 = 2H_2O + \widehat{NO}$. As both reactions occur instantaneously, they are written as one: $3Zn + 8HNO_3 = 3Zn(NO_3)_2 + 4H_2O + \widehat{2NO}$.

179. Exceptions.—Of the four common metals not dissolved by HNO_3 , Au and Pt are unaffected, Sb and Sn are changed to insoluble white metantimonic and metastannic acids; but if the acid is very dilute a little Sn will dissolve as $Sn(NO_3)_2$. Nitrates of Au, Pt, Sb are not known.

180. Nitrates.—From the above considerations it will be seen that nitrates are soluble (Table A). This can further be ascertained by adding HNO_3 to solutions of metallic salts, *e.g.*, chlorids, in separate beakers. No precipitate will form in any case. $Bi(NO_3)_3$ and to a less extent $HgNO_3$ and $Hg(NO_3)_2$ react with H_2O when a solution is attempted, and the basic nitrates, as $BiNO_3(OH)_2$ (variable), which are insoluble, are formed. The precipitates may be dissolved by adding HNO_3 . $Bi(NO_3)_3 + 2H_2O = BiNO_3(OH)_2 + 2HNO_3$. Metallic nitrates are formed by dissolving in HNO_3 either the metal or some compound of it, such as the oxid, hydroxid, carbonate, sulfid, etc. A typical reaction for the sulfid is $3CuS + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + \widehat{3S} + \widehat{2NO}$.

181. Oxidation.—Nitric acid oxidizes even non-metallic elements. So great is the affinity of phosphorus for strong HNO_3 that brilliant combustion—often explosion—ensues, and H_3PO_4 is formed, when a piece of phosphorus is put into the acid. This experiment must not be tried unless great caution is used. HNO_3 also transforms sulfur into H_2SO_4 , and iodine into HIO_3 , sets fire to hot charcoal or cold turpentine, and reacts

vigorously with benzene. It changes cotton into explosive gun-cotton, glycerin into nitroglycerin, and paper into a substance from which celluloid is made.

By reason of its oxidizing power it decolorizes organic pigments like indigo, $C_{16}H_{10}N_2O_2$, converting the latter into reddish isatin, $C_8H_5NO_2$. It stains animal matter yellow, *e.g.*, feathers, quills, finger nails, flesh, and white silk. The product formed is called xanthoproteic acid, and the color is best brought out by putting a little NH_4OH on the product. On passing HNO_3 through a red-hot tube it breaks up into H_2O , NO_2 , and O . Most nitrates, except those of the alkali and alkaline earth metals, break up similarly by action of heat, as $Pb(NO_3)_2 = PbO + 2\overbrace{NO_2} + \widehat{O}$.

182. Tests.—Some of the tests of nitric acid are: (1) It has a characteristic and stifling odor. (2) It acts on animal substances, turning them yellow. (3) It forms with copper a blue copper nitrate, and evolves dense red-brown fumes. (4) It decolorizes indigo solution. (5) With Sn it forms metastannic acid, but dissolves most other metals. (6) With ferrous sulfate it forms a brown ring or halo. This salt, with sulfuric acid, is a test for nitrates.

Exp. 87.—(1) Hold the end of the retort (Exp. 86), while gas is still escaping, over a few drops of NH_4OH in a dish or beaker. (2) Pour a few drops of the acid into an evaporating dish, and dip into it a piece of blue litmus paper. (3) Use a stirring rod and place a drop of it on the finger nail, or on a quill or feather, then wash it off, and put on a drop of NH_4OH . (4) Pour a few drops on some copper turnings. (5) Pour a few drops into a test tube containing some indigo solution. (6) Try to dissolve a little marble, $CaCO_3$, or CuS with it. (7) Put a drop on newspaper and on writing paper. This shows a test for wood pulp.

Exp. 88.—Put three or four crystals of $Pb(NO_3)_2$ into a test tube, heat it, and meanwhile thrust a lighted or glowing splinter into the tube.

Exp. 89.—Mix a very little of some nitrate, *e.g.*, $Pb(NO_3)_2$, with powdered charcoal, transfer to a dry test tube, and heat it.

Exp. 90. — Mix in a test tube a solution of some nitrate, *e.g.*, NaNO_3 , with a fresh solution of FeSO_4 , and when it is cold introduce with a glass used as a pipette (Fig. 68) to the very bottom of the tube a drop or two of H_2SO_4 . Let it stand, and watch the surface of contact between the acid and the liquid. A brown ring is formed.

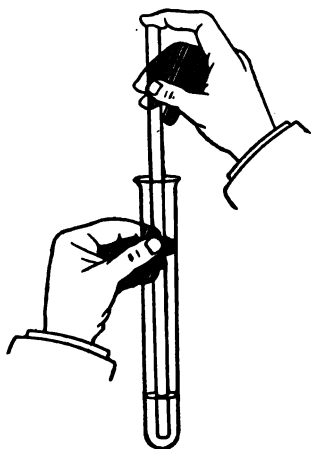


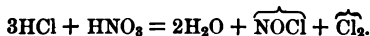
FIG. 68.

183. Uses. — The main uses of HNO_3 are to make nitrates, sulfuric acid, nitrobenzene, gun-cotton, nitroglycerin, celluloid, and in the laboratory to prepare aqua regia, dissolve precipitates, and oxidize substances. The

most important nitrates are those of K, Na, Ag, Ba, Sr, Bi; also nitroglycerin and gun-cotton. KNO_3 is used in gunpowder, NaNO_3 in making HNO_3 , AgNO_3 in photography, analysis, indelible inks, and hair dyes, $\text{Ba}(\text{NO}_2)_2$ and $\text{Sr}(\text{NO}_3)_2$ in fireworks, $\text{BiNO}_3(\text{OH})_2$ in medicine.

AQUA REGIA.

184. Aqua Regia (meaning *royal water* or *the king of liquids*, because when named it was the strongest solvent known) is not, strictly speaking, an acid, though often called nitro-hydrochloric acid. It is made by mixing two acids, nitric and hydrochloric, — 3 volumes of the latter to 1 of the former. A reaction takes place by which chlorin, nitrosyl chlorid, NOCl , etc., are formed and dissolved in the liquid, turning the color orange red.



Both Cl and NOCl are gases and attack most metals (even such as are not soluble in either HCl or HNO_3 separately), forming chlorids. The action is very vigorous, especially if the liquid is hot. The strength and solvent action is due mainly to the free chlorin. Gold and platinum are not affected by either HCl or HNO_3 , but they dissolve in aqua regia. Mercury and copper (which are soluble in HNO_3 but not in HCl) form with it the higher chlorids HgCl_2 and CuCl_2 . $\text{Au} + 3\text{Cl} = \text{AuCl}_3$. $\text{Hg} + 2\text{Cl} = \text{HgCl}_2$. Aqua regia is one of the strongest oxidizing agents, changing, *e.g.*, Hg' to Hg'' , Fe'' to Fe''' , etc. It has a strong, irritating, and characteristic odor, and reddish yellow color, due to a mixture of Cl and NOCl. It cannot be kept (since chlorin gradually reacts with water to form HCl), but must be made as wanted.

Exp. 91. — Pour into a test tube 6^{cc} of HCl and 2^{cc} of HNO_3 . If there is no action, or evidence of change, heat the mixture a moment.

Exp. 92. — (a) Pour a little of the aqua regia upon a few copper turnings in an evaporating dish. (b) Pour some on to zinc in a tube. What gas, if any, is liberated? (c) With a moist stirring rod put a piece of gold leaf into some aqua regia. (d) See whether gold leaf will dissolve in HCl or HNO_3 separately.

Exp. 93. — (a) Try to dissolve a little HgCl in aqua regia. (b) Add a few drops of aqua regia to some FeSO_4 solution, and boil it, then add NH_4OH . (c) Add NH_4OH to FeSO_4 solution, without HNO_3 . Compare the last two results.

CHAPTER XVI.

SULFURIC ACID.

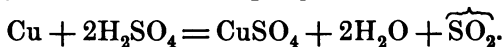
185. Sulfuric acid has been called, next to human food, the most valuable of products. Its manufacture is the basis of almost all chemical industries. It is used in enormous quantities in the preparation of material for bringing food-plants to maturity, in the manufacture from common salt of a great variety of compounds of sodium and of chlorin, which enter into the making of such substances as glass, soap, bleaching powder, and bread. Scarcely any of the products of civilized life have been brought to perfection without the use, directly or indirectly, of sulfuric acid. The progress of a nation in science, art, and civilization may be estimated by the amount of this acid used. Probably a million tons are made every year in Great Britain alone, much of which is shipped to other countries.

186. History.—Geber made and used this substance, which he called vitriolic acid, but Basil Valentine first described its preparation by distillation of FeSO_4 , and also by burning sulfur with nitre. The first process gave *fuming* sulfuric acid, $\text{H}_2\text{S}_2\text{O}_7$. When first made in England, in the middle of the eighteenth century, glass globes of 40 or 50 gallons' capacity with a little water in the bottom were used, and in these globes a red hot iron ladle was placed (resting on an earthen pot). Into this ladle was dropped a mixture of sulfur and nitre, then the whole was covered. In 1746 lead chambers of small size were substituted for this crude apparatus, and subsequently the chambers have been greatly enlarged.

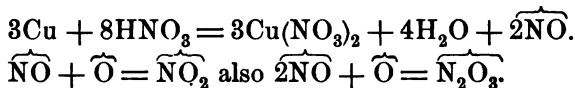
Names. — Hydrogen sulfate, hydric sulfate, sulfuric acid, oil of vitriol.

187. Occurrence. — In the spring waters of volcanic regions and in a few other springs very small quantities of the acid occur free, but owing to its strong affinities this is extremely rare. Its compounds — sulfates — are quite abundant and widely diffused. The most common are gypsum, CaSO_4 , barite, BaSO_4 , celestite, SrSO_4 , also, in certain springs, Epsom salt, MgSO_4 , and Glauber's salt, Na_2SO_4 .

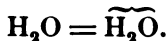
188. Preparation. — The manufacture of this valuable product depends upon a very simple principle. It is not practicable to make the acid from its salts. *Sulfur dioxide, SO_2 , in presence of H_2O and some oxidizer becomes H_2SO_4 .* SO_2 and H_2O have affinity for each other and form H_2SO_3 , which needs only one more oxygen atom per molecule to make it H_2SO_4 . If O were forced through the H_2SO_3 , or if the latter were exposed to the air, a weak acid would very slowly form, but in practice a stronger oxidizer is needed. HNO_3 , N_2O_3 , and NO_2 are most effectual for this purpose. Fig. 69 illustrates the preparation in the lecture room. SO_2 is made by the reducing action of Cu on H_2SO_4 .



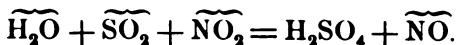
By the action of Cu on HNO_3 nitric oxid, NO, is formed, and this in presence of air oxidizes to NO_2 and N_2O_3 .



Steam is furnished by boiling water.



The gases thus formed, H_2O , SO_2 , NO_2 , mingle in the large central flask, and combine as follows :



Exp. 94. — Arrange an apparatus as in Fig. 69, having 3 small flasks

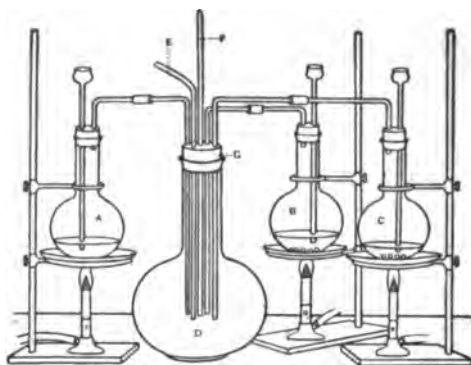


FIG. 69.

and one large central flask or receptacle. The stopper *G*, of the central one *D*, must be loose to allow the escape of gases, and a fourth opening at *E* is for forcing in air. *F* is a safety tube. Put water into one of the flasks, *A*, and boil it; into another, *B*, put copper turnings and H_2SO_4 , and heat this; and into the third, *C*, put copper turnings and HNO_3 ,

(diluted with half water). Heat the latter now and then, to make the oxids of nitrogen.

Explanation. — The effect is seen in the change from red NO_2 to colorless NO in the central receiver. Air must be forced in by a bellows or the mouth at *E*, and the fumes should be made alternately red and colorless, the lamps being manipulated for this purpose. The stopper for this receiver must be very loose or have openings, to allow the escape of extra gases. It will be seen that NO takes O from the air, being thus oxidized to NO_2 and N_2O_3 , and these give up O to H_2SO_3 to form H_2SO_4 , being themselves reduced to NO , which is again oxidized and the product again reduced. NO is said to be “a carrier of oxygen.” NO acts as a reducer and NO_2 as an oxidizer. For the laboratory, Exps. 95 and 96 are better adapted.

Exp. 95. — Burn a little sulfur in a receiver nearly closed with a glass plate, then pour in 5 or 10^{cc} of water, and at once suspend a stiff paper dipped into some HNO₃ in the fumes of the receiver. Leave it for a few minutes and watch the phenomena, take out the suspended paper and shake the contents of the bottle. Test the liquid (Exp. 98).

Exp. 96. — Burn sulfur in a receiver, then pour in 5 or 10^{cc} of hydrogen dioxide, H₂O₂, and shake the contents. Test the product.

189. Manufacture. — Sulfur is the basis of sulfuric acid. It was formerly obtained mainly from the island of Sicily, but now the common mineral *pyrite*, FeS₂, owing to its cheapness, is a source of the element. The manufacture of the acid on a large scale should be studied carefully, in connection with Fig. 70. A sulfuric acid plant is an extensive affair,

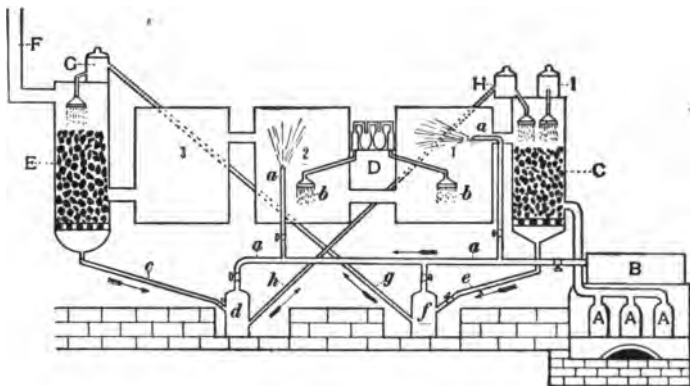


FIG. 70.

covering sometimes several acres. The pyrites, FeS₂, are burned in pyrites burners (A) with access of plenty of air, Fe₂O₃ and SO₂ being formed. $2\text{FeS}_2 + 11\text{O} = \text{Fe}_2\text{O}_3 + 4\widehat{\text{SO}_2}$. The heat also generates steam in the boiler B, and this passes through the pipes *aa* into the chambers 1, 2. SO₂ gas goes into the Glover tower, C, thence to chamber 1, where it mingles with the steam and the nitric acid (made at D from NaNO₃ and H₂SO₄) which passes in (at *b*). Some of the HNO₃ is decomposed by the heat into N₂O₃ and H₂O. These substances combine to form H₂SO₄. $\widehat{\text{SO}_2} + \text{H}_2\text{O} = \text{H}_2\text{SO}_3$. $\text{H}_2\text{SO}_3 + \text{HNO}_3 = \text{H}_2\text{SO}_4 + \text{HNO}_2$. $2\text{HNO}_2 = \text{H}_2\text{O} + \widehat{\text{N}_2\text{O}_3}$. The last two equations combined give

$2\text{H}_2\text{SO}_3 + 2\text{HNO}_3 = 2\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \widehat{\text{N}_2\text{O}_3}$. The excess of gases passes to chamber 2, where similar reactions occur. There are usually several connected chambers, each often 100 feet long and proportionately wide and high. They are lined with lead and called lead chambers, this being the only common metal which the acid will not attack. Finally the remaining gases are conducted into the Gay Lussac tower, *E*, and thence out of the tall chimney *F*. The chimney serves to make a draft for the gases as they enter the Glover tower and pass through the various chambers. At last not much gas except nitrogen escapes.

But this is not the whole process. Above the Gay Lussac tower is a tank, *G*, of comparatively strong H_2SO_4 , and above the Glover tower is one of nitrated H_2SO_4 , *H*, and another of water, *I*. These towers contain coke or fire brick loosely thrown in, so as to allow the liquids from the respective tanks to trickle down and absorb as much as possible of the ascending gases. In the Gay Lussac tower these gases are mainly N_2O_3 , and in the Glover tower SO_2 . N_2O_3 combines readily with strong H_2SO_4 (or dissolves in it) as the two mingle in the Gay Lussac tower, forming a so-called nitrated acid, which flows through the pipe *c* to the reservoir *d*, whence it can be forced by steam (through *h*) up to the reservoir *H*. This nitrated acid yields up its absorbed N_2O_3 as it meets in the Glover tower with SO_2 fumes from the pyrites retorts, H_2O from *a*, and *O* from the air, the combination forming H_2SO_4 , and so much of it that it is called strong acid. $\widehat{\text{N}_2\text{O}_3} + 2\widehat{\text{SO}_2} + \widehat{\text{H}_2\text{O}} + \widehat{2\text{O}} = 2\text{HNOSO}_4$. $2\text{HNOSO}_4 + \text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + \widehat{\text{N}_2\text{O}_3}$. It should be noted that HNOSO_4 (nitro-sulfuric acid) has the nitrosyl radical NO in place of one *H* atom in H_2SO_4 . N_2O_3 and NO_2 are both red gases and not easily distinguishable. Both are probably formed, though the above reactions give but one. The last N_2O_3 takes up more SO_2 , etc., and the process is continuous. The acid formed in the Glover tower flows through *e* to the reservoir *f*, whence it may be forced by steam again through *g* to the Gay Lussac tank, *G*, or drawn off. Thus the Gay Lussac tower is for collecting the nitric fumes in H_2SO_4 , and the Glover tower serves to separate the same fumes and mix them with SO_2 , H_2O , and *O*. Made thus, the acid is termed chamber acid, has a specific gravity of 1.5, and is about 65% acid and 35 water. This is strong enough for the manufacture of sulfate of soda, Na_2SO_4 , one of its two main uses. If stronger, it absorbs much N_2O_3 . It is then removed from the chambers and reservoirs, and evaporated in open lead pans till a specific gravity of 1.75 is obtained. Stronger than this it dissolves considerable lead, and it is then evaporated in platinum crucibles till the specific gravity is 1.83. This is about the commer-

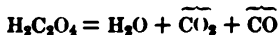
cial strength. Pure acid is 1.854. At the sulfuric acid works a large number of other products are usually made, *e.g.*, HCl, HNO₃, Na₂SO₄, Na₂CO₃, alum, and other sulfates, also nitrates and chlorids.

The question is often asked why sulfuric acid must be used to make the same acid, and how the first acid was made. It can be made without the use of sulfuric acid, as explained above, but the method is not practicable, and the amount of acid used is small in comparison with that obtained, though in lecture-room experiments it is large. A small quantity of the acid can be made by mixing SO₂ with hydrogen peroxid, H₂O₂.
$$\text{H}_2\text{O}_2 + \text{SO}_2 = \text{H}_2\text{SO}_4.$$

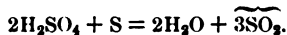
190. Properties. — *Physical.* It is a thick, heavy, oily, sour, and corrosive liquid, without odor or color if pure. It boils at 338° and freezes at about 0°.

Chemical. It has an acid reaction, is miscible in water in all proportions, the mixture becoming at first intensely hot, and when cool occupying less volume than the sum of the two liquids. At a red heat it dissociates into SO₃ and H₂O, and at a higher temperature into SO₂, O, and H₂O. The brown color of commercial acid is due to suspended particles of carbon. Most organic matter is blackened by it. Exposed to the air it absorbs moisture, and will often dilute itself to twice its original volume. It neutralizes the strong bases, and dissolves most of the metals, forming sulfates and liberating either H or SO₂, the latter from concentrated acid. Au and Pt are not affected by it. Much of its chemical activity is due to the great affinity it has for H₂O. Several organic compounds contain H and O in the right proportion to form water, *e.g.*, sugar, C₁₂H₂₂O₁₁, starch, and cellulose (C₆H₁₀O₅)_x. In contact with these, sulfuric acid abstracts the water and combines with it, leaving the carbon as a black mass.

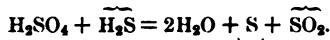
It also takes from oxalic acid, H₂C₂O₄, or alcohol, C₂H₆O, a part of the H and O, causes them to combine to form H₂O, and absorbs the latter.



Its action on the skin, making painful sores, and on organic matter generally, is due to its affinity for water. S, C, H₂S, and many other reducers form with it SO₂.



Zinc with hot, strong acid forms some H₂S, and this reacts on the H₂SO₄, liberating SO₂.



It readily transposes almost all salts, forming the corresponding acids and metallic sulfates. Sulfates are soluble, except those of Ba, Sr, Pb (Ca slightly). They are made by the action of the acid on the metals or their salts. Sulfates are bibasic, hence there are two classes, — the acid or primary (*e.g.*, HNaSO₄), and the normal or secondary (*e.g.*, Na₂SO₄).

191. Tests. — (1) H₂SO₄ put on writing paper and evaporated, chars, rots, and blackens it. (2) It also blackens wood, starch, or sugar, by extracting water and leaving charcoal, both of which result from their decomposition. (3) Added to BaCl₂ solution it forms a white precipitate of BaSO₄ insoluble in HCl. This becomes a test for any sulfate in solution, and is so delicate that a drop of the acid gives a visible precipitate in a liter of water with a little BaCl₂ solution. All other salts of barium, except the sulfate, are dissolved by dilute HCl.

Exp. 97. — (1) Place a drop of sulfuric acid with a stirring rod on writing-paper, and evaporate it so as not to burn the paper. See whether the paper is charred, blackened, or made rotten. (2) Pour a few drops of concentrated acid upon 1 or 2^g of sugar in a dish. (3) Dip a splint into a test tube containing 1 or 2^{cc} of H₂SO₄. (4) Pulverize a bit of starch, add a few drops of the acid, and cautiously heat it for a minute.

Exp. 98. — (1) Add a very little H₂SO₄ to 5 or 10^{cc} of BaCl₂ solution in a test tube. If a precipitate falls, add some dilute HCl and shake them well. If the precipitate does not dissolve, it shows a sulfate was present. (2) Make the experiment, using some other sulfate, *e.g.*, Na₂SO₄ solution, in place of H₂SO₄. (3) Into a liter of water in a large beaker pour a few cubic centimeters of BaCl₂ solution, then add one drop of H₂SO₄ and stir it well.

Exp. 99. — Into a small beaker $\frac{1}{2}$ full of H_2O pour slowly, with stirring, the same volume of concentrated H_2SO_4 , using for a stirrer a very small test tube partly filled with ammonium hydroxid. The heat will boil the NH_4OH .

Exp. 100. — Measure accurately 10^{cc} of water, and cautiously pour into it 10^{cc} — measured — of H_2SO_4 . When the mixture is cool measure its volume.

Exp. 101. — Measure out exactly 10 or 20^{cc} of H_2SO_4 and leave it in an open beaker for a week, then measure it again.

Exp. 102. — Add a little H_2SO_4 or solution of Na_2SO_4 to separate solutions of $\text{Pb}(\text{NO}_3)_2$, SrCl_2 , CuCl_2 .

192. Uses. — The sulfuric acid manufacture is the king of chemical industries. The acid is the basis of the manufacture of most other acids, and so of most salts. The manufacture of alkalis too, including sodium carbonate, depends mainly upon this acid. Only a few of the large number of uses can be given here. The two main ones are: (1) Its action on bones to make fertilizers. This action transforms an insoluble calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, into a soluble one, $\text{H}_4\text{Ca}(\text{PO}_4)_2$, thus enabling plants to absorb the phosphate from soils on which the fertilizer is used. Food plants like the cereals will not come to maturity or fruitage without phosphorus in this form. In this way our daily bread is in part supplied by H_2SO_4 (see Chap. XXX). (2) The second great use is in the preparation of sodium sulfate, Na_2SO_4 , from NaCl as a step in the sodium carbonate, Na_2CO_3 , manufacture (Chap. XXXIII). Carbonate of soda forms the basis of such industries as that of glass, soap, saleratus, baking powders, and most alkalis. Besides these uses sulfates are formed by action of the acids on metals or their salts.

Directly or indirectly H_2SO_4 is employed in the preparation of compounds for bleaching, dyeing, printing, electroplating, telegraphy, galvanizing iron plates and wire, cleaning metals, making shoe-blackening, glucose, mineral waters, soda water, ether, nitroglycerin, gun-cotton, vegetable parchment, celluloid, etc.

CHAPTER XVII.

AMMONIUM HYDROXID AND AMMONIA.

193. On an oasis in the north of the desert of Sahara stood a temple dedicated to Jupiter Ammon. This was the resort of caravans, and from the deposits of camels were obtained ammonia — named from the temple — and ammonium chlorid, NH_4Cl . Another name, spirits of hartshorn, given to the gas NH_3 at a later date, shows its preparation by distillation from horns and hoofs of deer and other animals. Though obtained now in a different way, most animal as well as vegetable matter in its decay gives rise to the formation of this compound of nitrogen and hydrogen, and for this reason it has been called a *post mortem* product. It has even been extracted from the mud of rivers such as the Thames.

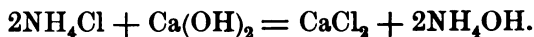
194. History. — Ammonia and some of its salts were known to the early alchemists. Geber was acquainted with the chlorid — then called sal-armoniacum. Basil Valentine (fifteenth century) showed that the gas could be made as we make it to-day from NH_4Cl . Priestley, 1774, first separated the gas, collecting it over mercury. He called it alkalin air, and also decomposed it by the electric spark. Berthollet, 1785, showed that it is composed of N and H, and Davy, 1800, made the volumetric determination.

Names. — Ammonia, hartshorn, liquor ammoniae, ammonium hydrate, ammonic hydrate, ammonium hydroxid.

195. Occurrence. — Ammonia is found free in small quantity only. A very little is formed, during electrical discharges in the air, from the hydrogen of water and nitrogen of air. This often combines with an oxid of

nitrogen (formed by the same process) to make NH_4NO_2 , ammonium nitrite, a small constituent of the air, and the product is finally washed by rain into the earth. Ammonium salts are volcanic products, and are also found as nitrites and nitrates in soils. The most important commercial compound is the chlorid, NH_4Cl . NH_3 is evolved in the distillation of bones and other animal tissues and excretions, and of coal and nitrogenous vegetable products in general.

196. Preparation. — The hydrate is prepared by the action of a strong base on one of its salts. The chief salts are NH_4Cl , NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{CO}_3$. By mixing any one of these with either $\text{Ca}(\text{OH})_2$, KOH , or NaOH and applying gentle heat, there are formed NH_4OH and NH_3 . Sal ammoniac, NH_4Cl , and slaked lime, $\text{Ca}(\text{OH})_2$, because of their cheapness, are usually employed.



It should be noted that the hydrate is only the gas combined with water, and the two substances, NH_4OH and NH_3 , are both called *ammonia*, but not accurately so. Wherever one of them is found the other usually exists, as NH_4OH gives off the gas, and NH_3 takes up water.

197. Manufacture. — On a large scale this base is made mostly from the ammoniacal liquor of gas houses, which results from the destructive distillation of soft coal. This liquor contains dissolved some $(\text{NH}_4)_2\text{S}$, $(\text{NH}_4)_2\text{CO}_3$, etc., and when treated with HCl , HNO_3 , H_2SO_4 , it gives the salts NH_4Cl , etc., and from these salts *liquor ammoniae* is obtained. Great quantities of the gas are formed in the preparation of coke in the iron regions.

Exp. 103. — Mix about equal portions of ammonium chlorid, NH_4Cl , and calcium hydrate, $\text{Ca}(\text{OH})_2$ — freshly slaked lime. Put 15 or 20^{cc} of the mixture into a flask and add a little water. Connect the flask with Wolff bottles (Fig. 71) and apply heat for 15 or 20 minutes. Disconnect the apparatus at *a* and apply the HCl test.

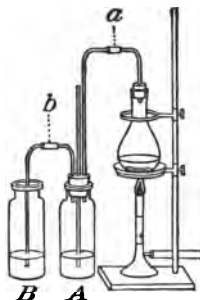


FIG. 71.

Exp. 105. — Put into an open test tube some salt of ammonium, and pour over it some NaOH (or KOH) solution. Heat the mixture and apply the tests for NH_3 .

198. Properties. — *Physical.* NH_3 is a colorless gas, having a very pungent odor and acrid taste. It is extremely soluble in water, for which it has great affinity. A liter of water at 0° will dissolve 1148 liters of the gas, and considerably increase in volume. It can be liquefied and solidified by cold and pressure. The evaporation of liquid NH_3 produces cold sufficient to freeze water.

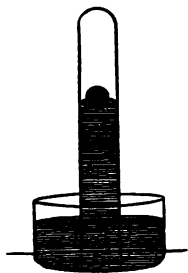


FIG. 72.

Fig. 72 shows how freely charcoal absorbs NH_3 . The tube is first filled with NH_3 and inverted over mercury; then a piece of freshly calcined charcoal is put into the tube. The gas is rapidly absorbed into the pores of the charcoal, and mercury rises to take its place.

Chemical. NH_3 does not support ordinary combustion, nor does it burn in air, but in pure oxygen it burns with

a pale yellow flame (Fig. 73). The combination of NH_3 with H_2O gives NH_4OH . Whether there is a definite com-

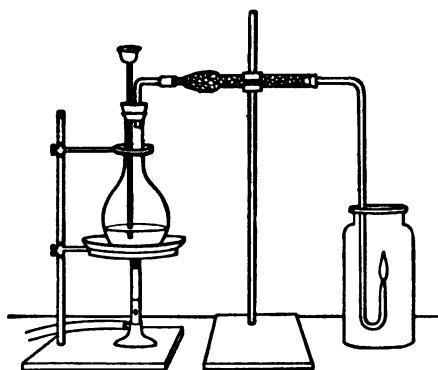


FIG. 73.

compound of that composition is still a little uncertain, but the evidence is in favor of it. It forms insoluble hydrates such as $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, etc., the same as KOH does, from solutions of ferric and aluminum salts, *e.g.*, FeCl_3 , $\text{Al}_2(\text{SO}_4)_3$, etc.

NH_4OH is strongly alkaline, coloring red litmus, red logwood, etc., blue, and it combines with acids to form salts.

It is a curious fact that an electric discharge in a mixture of N and H in a tube will form minute quantities of NH_3 , whereas a strong discharge acting on the compound NH_3 breaks it up into its elements. If in the first case some H_2SO_4 is used to absorb the NH_3 as fast as it forms (Fig. 74) and the "sparking" is continued, all the N and H will finally combine — supposing the gases to be proportionately mixed. If no absorbent is used, only a little NH_3 is formed. Ammonia is also decomposed at 780° by passing it through a red-hot tube.

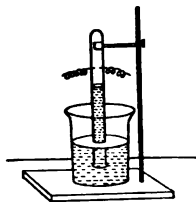


FIG. 74.

199. Artificial Ice. — Fig. 75 represents Carré's freezing apparatus. The cylinder *A* is connected by tubes with *E*, which contains an inner cylinder, *C*, that slides into *D*. *D* is surrounded by a jacket, *E*.

Into *A* is poured NH_4OH . *C* is filled with water to be frozen, and is then fitted into *D*. *B*, containing *E* and *C*, is placed in cold water and *A* is heated to evaporate NH_3 , which passes into *E* and is there liquefied by the cold and its own pressure. *B* is then taken out of the water, the heat is removed from *A*, and *A* is put into cold water. This causes the liquefied NH_3 to vaporize and pass back from *E* into *A* so rapidly that it withdraws heat enough to freeze the water in *C*.

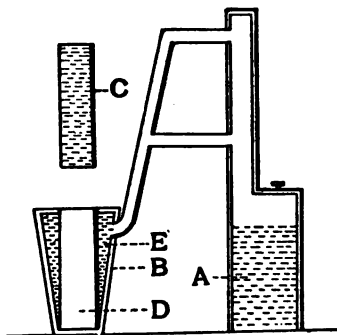


FIG. 75.

200. Tests. — NH_3 is tested (1) by its odor, and (2) by the formation

with HCl of dense, bluish white fumes of NH_4Cl . (3) The hydroxid gives precipitates in solutions of salts of Al , Fe , Cr , etc. (4) Nessler's solution detects one part of NH_3 in 100,000,000 parts of water. (5) Copper sulfate paper is turned blue by NH_3 , (6) mercurous nitrate paper is turned black.

Exp. 106. — Test the liquid in the Wolff bottles (Exp. 103) with litmus, note the odor, and add some to each of these solutions: FeSO_4 , FeCl_3 , AlCl_3 , CuCl_2 (very little, then excess).

Exp. 107. — Collect a test tube full of NH_3 by upward displacement, (heating some NH_4OH in a flask), and at once put the mouth of the inverted tube under water. Hold it there and see whether water rises.

Exp. 108. — Try to burn NH_3 in O , as in Fig. 73. Heat NH_4OH gently in the flask, and pass O into the receiver. Lower the jet of NH_3 into the receiver of O and light it as it enters.

Exp. 109. — Collect a receiver of NH_3 by upward displacement, and put in a stopper through which passes a tube drawn at one end to a small opening (Fig. 76). Quickly immerse the other end of the tube in a beaker containing a solution of litmus colored red by one drop of HCl . The liquid may be forced up in a jet, and colored blue by the NH_3 which it absorbs.

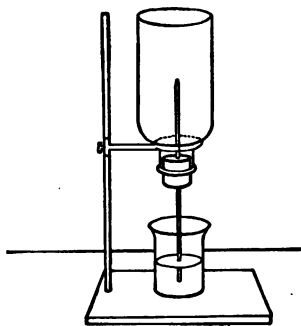


FIG. 76.

Exp. 110. — Wind a Pt wire into a spiral, attach it to a copper wire, and fit the latter so as to hang into a flask, into which a few drops of NH_4OH have been poured. Shake the liquid well and then heat the Pt wire red hot and hang it in the receiver near the bottom (Fig. 77). Fumes of N_2O_3 (red) and NH_4NO_2 (white) will be seen as the wire continues to glow.

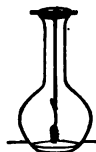


FIG. 77.

$$2\text{NH}_3 + 6\text{O} = \text{N}_2\text{O}_3 + 3\text{H}_2\text{O}. \quad \text{N}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{HNO}_2. \quad \text{HNO}_2 + \text{NH}_3 = \text{NH}_4\text{NO}_2.$$

Exp. 111. — To a little dilute NH_4OH add a few drops of Nessler's solution.

Exp. 112. — Test ammonia with unglazed paper dipped in CuSO_4 solution. Also in HgNO_3 solution.

201. Uses. — Ammonia finds many uses in medicine. Its compounds serve to furnish nitrogen, which is essential to the growth of both vegetable and animal life. Hence the use of ammonia in fertilizers for the soil.

CHAPTER XVIII.

HYDROXIDS OF SODIUM, POTASSIUM, AND CALCIUM.

THE FIXED ALKALIS.

202. The word *alkali* meant originally *ash*, a particular sort containing Na_2CO_3 , and used in glass-making. The source of alkalis was ashes of both sea plants and land plants. Two classes were early distinguished, — the mild alkalis, which we now call alkaline carbonates, as Na_2CO_3 , and the caustic alkalis, as NaOH . We now make two divisions of these latter, *viz.*, the volatile alkali NH_4OH , which on heating entirely vaporizes, and the fixed alkalis, which leave a solid residue on evaporating their solutions. There are two of these, — KOH and NaOH . With strong heat these vaporize but do not break up, and hence, until Davy's classic experiments on them with the electric current, they were regarded as elements. Both sodium and potassium hydroxids were called by one name, *potashes*, because derived from the ashes of plants by leaching them in pots, and not until 1736 were they distinguished from one another. In fact the properties and the mode of manufacture of both are nearly identical. KOH was originally obtained from the ashes of land plants, NaOH from those of sea plants, by treating the solutions with lime, Ca(OH)_2 .

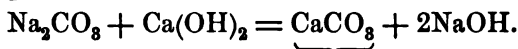
203. History. — Duhamel, 1736, distinguished NaOH from KOH . Black, 1756, distinguished by chemical means mild alkalis from caustic,

Davy, 1807, decomposed NaOH and KOH, and proved they were not elements.

Names.—Sodium (or potassium) hydroxid or hydrate, caustic soda (or potash).

204. Occurrence.—Owing to their strong affinities, neither KOH nor NaOH is found free. Potassium and sodium occur very commonly as silicates in granite and other rocks, and in their chlorids, NaCl and KCl, and other salts, but never free. Potash, K_2CO_3 , is the principal alkali of the animal body. The raw wool of sheep contains much potash.

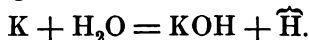
205. Preparation.—The hydroxids of both potassium and sodium are prepared from their carbonates, K_2CO_3 and Na_2CO_3 , by the action of calcium hydroxid, $Ca(OH)_2$.



Sodium carbonate is used in solution, which must not be too strong, or the lime will not act upon it. Lime is introduced as a solid, and the mixture is boiled. Insoluble carbonate of lime is precipitated, and the caustic alkali remains in solution, is filtered and evaporated. Made in this way it contains carbonates and other impurities. It is then called "caustic soda (or potash) by lime." The presence of carbonates in commercial caustic soda can be shown by adding a little HCl to a solution, when effervescence takes place. Alcohol will dissolve the alkali and leave the impurities. The alcoholic solution is filtered, evaporated in a silver dish, and the liquid alkali poured into moulds lined with silver, as this metal is not acted on by the hydroxid. When purified by this

process it is called "soda by alcohol." Lime will not act upon most compounds of sodium or potassium, as NaCl and K_2SO_4 , to form hydrates.

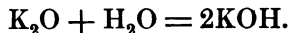
Sodium or potassium in contact with water decomposes it with violence, forming NaOH or KOH and liberating half of the hydrogen.



The action is so violent and the heat so great in the case of potassium that when exposed to the air both hydrogen and potassium are set on fire.



The oxid of potassium formed combines with water to make KOH .



It is necessary to heat the water to produce the same effect with Na .

Exp. 113. — To 5 or 10^{cc} of Na_2CO_3 solution, add as much lime water, $\text{Ca}(\text{OH})_2$ solution, and warm it. See whether there is a precipitate.

Exp. 114. — Take a rather weak solution (about 10%) of Na_2CO_3 (or K_2CO_3) in water, pour it into an evaporating dish or a beaker, and add freshly slaked lime. Boil the mixture for about ten minutes and then filter it. Test a little of the filtrate with dilute HCl and see whether it effervesces. Apply tests as in Exp. 118.

Exp. 115. — (a) Throw a piece of sodium into a receiver one-fourth full of water, and cover the receiver at once with paper or cardboard (Fig. 78). Watch the action, and when it stops try to light the gas in the receiver. Also at once hold the lower openings of a Bunsen burner, having the gas burning, over the mouth of the receiver (Fig. 79), and note the color imparted to the flame. Test the solution as in case of



FIG. 78.

NH_4OH . (b) Try the action of Na on hot water. (c) Float a wet filter paper on water and put a piece of Na on it.

Exp. 116.— Try the action of potassium on cold water, as in the experiment above, and test the color of the flame, which is due to compounds of potassium.



FIG. 79.

Exp. 117.— Collect a test tube full of hydrogen over water by placing a piece of Na in a wire cage (Fig. 80), immersing it in water under an inverted test tube of water.

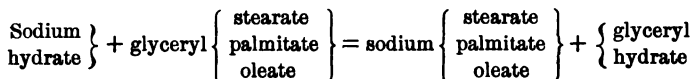


FIG. 80.

206. Properties.— *Physical.* The hydroxids of potassium and sodium are white solids, acrid and nauseating to the taste and very caustic, dissolving the flesh. KOH is the stronger, and in fact the strongest of bases. Both are deliquescent, absorbing from the air H_2O as well as some CO_2 , with which they gradually form K_2CO_3 and Na_2CO_3 . They are very soluble in water, as are most compounds of Na and K.

Chemical. They neutralize the strongest acids and thus form salts, they act upon most metals, and are powerful solvents of animal and vegetable matters. Only very dilute solutions can be filtered through paper. Their saponifying (soap-making) action depends upon the power to transform and dissolve fats and oils. KOH makes soft soap, NaOH hard. Na (or K) will combine with NaOH (or KOH) and form Na_2O (or K_2O). $\text{Na} + \text{NaOH} = \text{Na}_2\text{O} + \text{H}$.

207. Soaps. — Fats and oils are mainly stearin (or glyceryl stearate), $C_3H_5(C_{18}H_{35}O_2)_3$, palmitin (or glyceryl palmitate), $C_3H_5(C_{16}H_{31}O_2)_3$, and olein (or glyceryl oleate), $C_3H_5(C_{18}H_{33}O_2)_3$, C_3H_5 being the glyceryl radical. Glycerin (or glyceryl hydrate) is $C_3H_5(OH)_3$. In saponification the hydrate of sodium or potassium acts on the stearin, palmitin, or olein, and liberates glycerin, forming sodium stearate, etc.



The stearate, palmitate, and oleate of sodium or potassium are chemical names for soaps. They are soluble in water, hence a solution of NaCl — in which they are insoluble — is used to precipitate them.

Exp. 118. — (a) Test with litmus paper solutions of NaOH or KOH obtained in the last experiments. (b) Taste a *drop* from the finger or a stirring rod. (c) Add a little to solutions of each of these: (d) $FeSO_4$, (e) $FeCl_3$, (f) $AlCl_3$, (g) $CrCl_3$, (h) $NiCl_2$. (i) See whether any of the precipitates obtained are soluble in excess of strong NaOH or KOH solution.

Exp. 119. — Put a small piece of NaOH on a glass plate or in a dry evaporating dish and leave it till the next laboratory period.

Exp. 120. — Pour 10^{cc} of strong NaOH solution into an evaporating dish and add 3^{cc} of sweet oil. Boil the mixture, stirring it meantime till it becomes quite clear. Now add 3^g of NaCl, boil it a minute, and let it cool. Soap should collect on the top of the liquid.

208. Uses. — These hydrates are mainly used in soap-making. Considerable quantities are employed in the laboratory and some in surgery for cauterizing the flesh. Thousands of tons of caustic soda are made into soaps each year.

CALCIUM HYDROXID.

209. The most abundant and most useful of the bases is calcium hydroxid $Ca(OH)_2$, the common name of which

is *lime* or slaked lime. It may be said to stand in somewhat the same relation to other bases that H_2SO_4 does to acids. It is used to make alkalis and hence might be called the strongest base, as H_2SO_4 is often called the strongest acid. But the chemical strength of an acid or base depends as much on the substance to which it is applied as on itself, and for most purposes lime is not regarded as a strong base. Sulfuric acid is not made directly from its salts, but has to be synthesized, and calcium hydrate is also made by an indirect process.

210. History.—In ancient times, as described by Pliny, lime was “burned,” slaked, and used to make caustic potash and soda, and also for mortar, as it is to-day.

Names.—Calcium hydroxid, calcium hydrate, lime, slaked lime are all $\text{Ca}(\text{OH})_2$. Quicklime, or unslaked lime, is CaO . Limestone, or carbonate of lime, is CaCO_3 . Marble is finely crystallized limestone. Calcite is also CaCO_3 in crystals. Lime water is $\text{Ca}(\text{OH})_2$ dissolved in water. Milk of lime and cream of lime are finely divided $\text{Ca}(\text{OH})_2$ suspended in water, more than will dissolve in it. Sulfate of lime is CaSO_4 .

211. Occurrence.—Lime itself does not occur free. The main source of it is calcium carbonate, a very abundant and widely distributed rock. Enough of this is said to be found in every state in the Union to pay for burning into lime. Some entire mountains and chains of mountains are composed of it. It is probably in all cases the product of early organic life. Great quantities exist in the sea. Corals, clam and oyster shells, and in general the shelly coverings of invertebrates are CaCO_3 . Coral reefs extend for thousands of miles in the sea and sometimes many hundreds of feet in depth. These deposits, which are the secretion of polyps, have in past ages been slowly depressed into the depths of the sea, or raised

into dry land, and from them, as well as from chalk, etc., we obtain our limestone and marble.

212. Preparation. — The first step in the preparation of $\text{Ca}(\text{OH})_2$ is called the “burning of lime.” A conical-shaped furnace built of brick and earthy material is filled with alternate layers of CaCO_3 and coal or wood, and the latter is set on fire (*A*, Fig. 81). The heat is enough to break up the CaCO_3 — which begins to dissociate at a red heat — into CaO and CO_2 . CO_2 escapes as a gas, and CaO remains as a hard, compact mass of quicklime, which is removed at *B*.

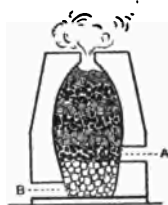


FIG. 81.



CaO must be packed in air-tight barrels and kept away from water.

The second step consists in “slaking lime.” This is done by pouring water on it. $\text{CaO} + \text{H}_2\text{O} = \text{Ca}(\text{OH})_2$. The heat generated by the union of water with quicklime is so great as to vaporize much of the water, and, if very large quantities are used, wood is often set on fire. If fire gets started where a great deal of lime is stored it is difficult to extinguish, for the more water that is used, the greater the heat. Most lime is “burned” where the CaCO_3 is quarried, but is “slaked” at the place where it is used for building purposes.

Exp. 121. — Put 10 or 20% of quicklime, CaO , in lumps, into an evaporating dish and pour over it a little H_2O . Add more H_2O from time to time — avoid excess — till vigorous action ensues. Describe the action and keep the product for the next experiments.

213. Properties. — CaO is a hard, compact, amorphous white (when pure) solid. It has great affinity for water, and forms with it slaked lime. During the process of slaking it becomes hot, swells, breaks open, and forms a powder. If excess of water is used some of the lime dissolves. If exposed to the air, CaO slowly takes up water and a little CO_2 , and slakes itself. This is called "air-slaked lime." It contains a little CaCO_3 . $\text{Ca(OH)}_2 + \text{CO}_2 = \text{CaCO}_3 + \text{H}_2\text{O}$.

214. Mortar. — Ca(OH)_2 is quite soluble in water, but not so soluble as NaOH . It is mixed with fine, sharp sand to form *mortar*, which is a cement for bricks, stone, etc. Mixed with sand and hair it makes plastering for house interiors. As mortar hardens, it loses water, the Ca(OH)_2 slowly combines with CO_2 of the air to make CaCO_3 , and also with the sand and clay of bricks to form calcium silicate, etc. These serve to cement together the bricks, which will often break more readily than they will separate from the mortar. Hydraulic mortar contains an excess of silica and is not affected by water.

Exp. 122. — Put some of the slaked lime, Ca(OH)_2 , from Exp. 121, into a receiver, fill the latter with H_2O , stir the mixture well, and let it stand for some time, then filter it. Test the filtrate to see whether any Ca(OH)_2 is in solution. (a) Try the litmus test — both colors. (b) Taste a drop. (c) Evaporate a few drops in an evaporating dish, and look for a residue. (d) Boil 5 or 10 cc of it in a test tube, and look for a precipitate. A little HCl will clean most of the adhering impurities.

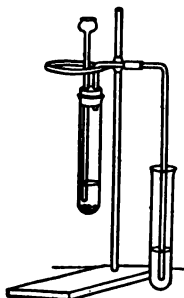


FIG. 82.

Exp. 123. — Pour 10 cc of Ca(OH)_2 solution (Exp. 122) into a clean test tube and pass CO_2 into it from a generator (Fig. 82), or blow through

a glass tube into it. Look for any precipitate. Explanation of this phenomenon is given under "Carbon Dioxid."

215. Uses. — The main use of lime is for making mortars and plastering. The amount of it consumed can be imagined from the number of buildings annually erected. A little is used in medicine and in laboratories. Its solution is employed as a test for carbonates.

CHAPTER XIX.

UNION BY VOLUME

216. Without Avogadro's Law of Gases it would be almost impossible to obtain the symbol of a compound. The "chemical theory" rests on this law. In theory we study the weight of atoms and molecules, as in practice we study the weight of liters of gases. In both cases it is the weight of volumes of gases. Here are two things which must be carefully distinguished, — *weight* and *volume*. A liter of oxygen and one of hydrogen have the same volume, yet the former weighs 16 times the latter, and a liter of iodine vapor weighs as much as 126 liters of hydrogen.

217. History. — The Italian physicist Avogadro announced this law in 1811, and the French physicist Ampère in 1814, but it took chemists half a century to apply it to symbols.

218. Avogadro's Law of Gases. — *Equal volumes of all gases — compounds as well as elements — have the same number of molecules, if the temperature and pressure are alike in both cases.*

This law cannot be proved or verified in the same way that the Law of Definite Weight can, for no one has ever seen or experimented with separate molecules; but, among other considerations, the fact that different gases all expand equally with a given rise of temperature and contract equally with a given fall of temperature, that they expand equally with

the removal of pressure, and contract equally with a given addition of pressure, has led to the conclusion that if gases have molecules at all, equal volumes must have equal numbers. What the number may be, is by no means certain. Various estimates have been made. Lord Kelvin estimated that the number per liter, at 0° and 760^{mm} , is represented by the 24th power of 10, i.e., 1 with 24 ciphers annexed. But the exact number is not necessary in order to ascertain symbols from known volumes, or volumes from symbols, or to solve volumetric problems.

219. Relative Weights. — *To obtain the relative weights of two different kinds of molecules, we must weigh equal volumes of the two gases.*

There are two conditions to this law : (1) In weighing two gases the temperature of the room must be the same for both, or the one weighed at the lower temperature will have the more molecules, since heat expands gases. A liter at 0° becomes 2 liters at 273° , and for each degree above 0° the volume is increased $\frac{1}{273}$. (2) Weighing of both must also be done under the same pressure. The greater the pressure the more molecules in a given volume. A liter of gas under pressure of one atmosphere becomes $\frac{1}{2}$ a liter under two atmospheres, and 2 liters under half an atmosphere. If two gases are weighed at the same time and in the same room, the temperature and pressure will be practically the same, but it is convenient to have a standard, and tables are made to reduce the weight at any temperature and pressure to 0° and 760^{mm} . The methods of weighing are described in Chap. XXVII. A standard gas is also employed. This is *hydrogen*, because of its being the lightest of all gases. It is evident that it makes no difference what volume of any given gas is weighed, provided the weight is compared with the weight of an equal volume of the standard, hydrogen.

220. From Liter to Atom.—If a liter of oxygen weighs 16 times a liter of hydrogen, a cubic centimeter of the former will weigh 16 times a cubic centimeter of the latter. Now since (Law of Avogadro) all molecular volumes are equal, the molecular volume of oxygen must weigh 16 times the molecular volume of hydrogen, and there is the same ratio of 16 to 1 between the half molecular volumes of each gas. *The half molecular volume of any gas is that volume which is equivalent to the volume of a hydrogen atom*, because there are two atoms (and two atomic volumes) in the hydrogen molecule, $\boxed{\text{o o}}$. How do we know this? The proof is as follows: Let us assume there are 100 molecules in a liter of hydrogen. A liter of chlorin will have the same number, 100 (Law of Avogadro). Suppose now the two gases combine; two liters of hydrogen chlorid will form. These two liters must contain 200 molecules of the gaseous product (Law of Avogadro). Now each molecule must contain *at least* one atom of hydrogen and one of chlorin, or two of both, and 200 molecules will have 400 atoms, half of which are chlorin and half hydrogen. There are then 200 atoms of hydrogen in the product, and hence in the factors. Since there are 200 atoms and 100 molecules in a liter of hydrogen there must be two atoms in each molecule ($200 \div 100 = 2$). There are *at least* two. There may be more, but cannot be less. We therefore assume the smallest number, 2. The same proof may be had by assuming the unknown number of molecules in a liter of each gas to be x . The number in the compound will be $2x$, each of which must contain 2 atoms, $4x$ atoms in all, $2x$ atoms of which are hydrogen, $2x$ chlorin. If x molecules consist of $2x$ atoms, then each molecule will

have 2 atoms. $2x$ atoms = x molecules \therefore 2 atoms = 1 molecule.

We see that it makes no difference whether we take for comparison the volume of a liter, of a cubic centimeter, of a molecule, or of an atom of the two gases, the relative weights will be the same. It is most convenient to take the smallest weight possible, *viz.*, the weight of the volume of an atom of hydrogen \square , because that is one-half the molecular volume of any gas. The hydrogen atom is the smallest particle of matter by weight known to science, hence its weight forms the unit of atomic and molecular weights, its volume the unit of atomic and molecular volumes, and the unit of vapor density (Chap. XXVII).

221. Application. — We will now see how this law applies to the symbols of certain compounds like HCl, H₂O, H₂N, H₄C. Experiments show that when hydrogen chlorid is formed, equal volumes of each element combine. A liter of hydrogen always combines with a liter of chlorin and forms two liters of hydrogen chlorid, — no more and no less. In the accompanying illustrations (p. 153) a large square stands for a liter of gas, a small one for an atomic volume, a double large one for two liters, a double small one for a molecular volume. The circles are the actual *essence* of the atoms, the parts which stand for *matter* and which determine the *weight* or *mass* of substances. Each molecule has a definite volume enclosed by planes which lie halfway between this molecule and its nearest neighbors. This volume we call the *molecular volume*. *All molecular volumes of gases are equal.* Each is represented by a double cube or double square $\square\square$, because the hydrogen molecule has two atoms and two atomic volumes, each of which is shown by a cube or by a square containing a sphere or a circle $\square\circ$. (See Chap. I.)

Now since one liter of hydrogen combines with one liter of chlorin to form two liters of hydrogen chlorid, .000001, *e.g.*, of a liter of hydrogen will combine with .000001 of a liter of chlorin to form .000002 of a liter of hydrogen chlorid. Whatever the number of molecules in a liter, — whether a million or more or less, — the contents of each molecular volume of hydrogen combine with the contents of each molecular volume

of chlorin to form what constitutes two molecular volumes of the product. The half molecular volumes of each factor unite to form the whole molecular volume of the product. But the half molecular volumes are atomic volumes with the contained atoms. Hence one atom of hydrogen combines with one of chlorin to form a molecule of hydrogen chlorid, or $\widehat{\text{H}} + \widehat{\text{Cl}} = \widehat{\text{HCl}}$.

In the second case, the symbol H_2O and the equation for its preparation, are explained in this way: Experiment shows that two liters of hydrogen combine with one liter of oxygen to form two liters (not three liters) of hydrogen oxid gas. It must be noted that there are not as many molecular volumes (and molecules) in the two liters of the product as in the three liters of the factors, because, by the law, two liters can have only two-thirds as many molecules as three liters. Hence two atomic volumes (and atoms) of hydrogen combine with one atomic volume (and one atom) of oxygen, to form two atomic volumes (or one molecular volume) of hydrogen oxid. Therefore $2\widehat{\text{H}} + \widehat{\text{O}} = \widehat{\text{H}_2\text{O}}$. Compare the small squares with the corresponding large ones. Three liters have contracted to two, hence three atomic volumes have contracted to two; but the two liters of the product weigh as much as the three of the factors, hence the two atomic volumes of the product weigh the same as the three in the factors, and, as this is the weight of the atom itself (represented by the circle) there must be the same number of actual atoms (not atomic volumes) in the product as in the factors. The atom itself is the one unchangeable thing. Whatever changes the substance undergoes, whatever new combinations are formed or old ones broken up, whatever contraction or expansion in volume, *the atom, by theory, is indestructible and unchangeable*. This gives us the clearest notion of the indestructibility and uncreatability of matter.

In the third case, three liters of hydrogen combine with one liter of nitrogen to form two liters of hydrogen nitrid, or ammonia. Since there is the same number of atomic volumes in a liter of each, three atomic volumes of hydrogen must have one atomic volume of nitrogen, and produce two atomic volumes of ammonia. Hence the relation must be as shown below, $3\widehat{\text{H}} + \widehat{\text{N}} = \widehat{\text{H}_3\text{N}}$. Four volumes have been reduced to two in the chemical union, without any loss of weight.

222. Condensation Ratio.—In the last illustration there was a contraction (or loss of volume) of one-half—i.e., a loss of two volumes out of every four. In the second case, where water was formed, there was a contraction of one volume in three—a condensation ratio of

one-third, which simply means that the volume of the product is two-thirds that of the separate factors. This assumes that the water is at the temperature of vapor, since liquid water occupies only about $\frac{1}{1800}$ part its volume as a vapor. In the case of HCl there was no contraction, the product having the same volume as the factors.

This law concerns only gases. We cannot reason from it with regard to the volume of liquids or solids. Still, all symbols are written as though the same were true of liquids and solids also. Take H_4C for example: we do not know what the volume of the carbon atom is, as carbon has not been vaporized, but we may assume that it has the usual volume. The symbol of a compound shows what is the condensation ratio in its formation from elements. C_2H_6O is a molecule of alcohol which occupies two atomic volumes. The elements before combination would occupy (assuming the volume of C as before) nine such volumes. The condensation ratio is therefore seven-ninths.

State and explain the condensation ratio in these symbols: HF, C_2H_2 , $(C_2H_5)_2O$, CH_4O . See whether by the application of the above principles and by drawing squares you can explain why the symbols HBr, H_2S , H_2O_2 , N_2O_3 are correct. *Algebraically* the above explanation may be formulated as follows:

- (1) 1^l hydrogen + 1^l chlorin = 2^l hydrogen chlorid, or
- (2) $\left\{ \begin{array}{l} x \text{ atomic vol-} \\ \text{umes of hy-} \\ \text{drogen} \end{array} \right\} + \left\{ \begin{array}{l} x \text{ atomic vol-} \\ \text{umes of} \\ \text{chlorin} \end{array} \right\} = \left\{ \begin{array}{l} 2 x \text{ atomic vol-} \\ \text{umes of hydro-} \\ \text{gen chlorid} \end{array} \right\} \quad \begin{array}{l} \text{Divide} \\ (2) \text{ by } x. \end{array}$
- (3) $\left\{ \begin{array}{l} 1 \text{ atomic vol-} \\ \text{ume of hy-} \\ \text{drogen} \end{array} \right\} + \left\{ \begin{array}{l} 1 \text{ atomic vol-} \\ \text{ume of} \\ \text{chlorin} \end{array} \right\} = \left\{ \begin{array}{l} 2 \text{ atomic vol-} \\ \text{umes of hydro-} \\ \text{gen chlorid} \end{array} \right\}, \text{ or}$
- (4) $\boxed{\circ} + \boxed{\bullet} = \boxed{\bullet \circ}$ or (5) $H + Cl = HCl$. Apply it in the other cases.

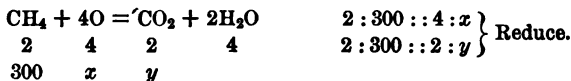
223. Reversal. — We have applied the Law of Avogadro to the synthesis of compounds, but it is equally applicable to the decomposition of compounds into their elements. The student should take such experiments as the electrolysis of water and apply the reasoning as above. Also the following: an electric spark passed repeatedly through 2^{cc} of ammonia increases the volume to 4^{cc} of a gas which proves on analysis to contain 3^{cc} of hydrogen and 1^{cc} of nitrogen. Explain how from this experiment Avogadro's Law determines the symbol of ammonia. The synthesis of substances to show volumetric relations by the eudiometer is explained in Chap. XX.

224. Application.—We may reason not only from experimental volumes of gases down to theoretical atomic volumes,¹ but may reason backward from atomic volumes to cubic centimeters or liters, and in this we find the practical application of the principles we have studied. Suppose we wish to know how many liters of oxygen gas are required to burn 5 liters of hydrogen. We proceed as follows, following the general plan given in Union by Weight, Chap. VI. (1) Write the equation. (2) Underneath write the atomic volumes, as shown by the equation. (3) Place the volumes indicated in the question, under the atomic volumes, putting x and y for the unknowns. (4) Make and solve the proportion. The above question is solved as follows :

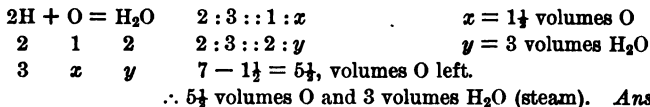


The question may be asked what right we have to compare, as in the above proportion, atoms with liters or cubic centimeters. Avogadro's Law shows that atomic volumes are only fractional parts of liters, hence the ratio of atoms (or atomic volumes) to liters is the same as that of fractions to whole numbers of the same kind.

Problems.—(1) How many cubic centimeters of oxygen will burn 300^{cc} of marsh gas, CH_4 , and how much CO_2 will form ?



(2) Three volumes of H are mixed with 7 volumes of oxygen and exploded over mercury. What volume of gaseous H_2O will form, and what and how much of either factor will be left over ? On writing the equation it is evident that not all the O can combine. It is solved thus :



¹ The terms *atomic volume* and *molecular volume*, as employed in this book, have a meaning different from that which has been accorded them by certain chemists. So far as the author is aware, the terms, as herein used, are original with him, and the apology for their use is that they seem essential to a clear exposition of Avogadro's Law, and of the deductions from it.

(3) How much O will it take to form 110^l of CO₂? (4) How many cubic centimeters of acetylene, C₂H₂, will it take to unite with 3^l of O? (5) 21 cu. in. of CO and 10 cu. in. of O are ignited. How many cubic inches of CO₂ result, and what is left? (6) Three liters of a mixture, in equal volumes, of CH₄, C₂H₄, and CO are burned, the products being CO₂ and H₂O. How much O is required and how much CO₂ formed? (7) C₂H₆ burns in oxygen. How much CO₂ by volume will 7^l of it form? (8) What relative volumes of a mixture of CH₄ and O would be most dangerously explosive? (9) Of CH₄ and air? (10) Of H₂S and air? (11) When alcohol vapor, C₂H₆O, burns in air what are the relative volumes of the 4 gases concerned in the reaction? (12) Write the volumetric proportions of factors and of products when CO burns in oxygen. Let the student be required to make up and solve several questions in Union by Volume.

CHAPTER XX.

OXIDS OF HYDROGEN AND OF OXYGEN.

225. We have now studied the great classes of compounds — acids, bases, and salts — together with some of the principles of chemistry, and four typical and important elements. Among the most important compounds of these four elements are oxids, and to these — the oxids of hydrogen, of carbon, and of nitrogen — we shall now direct our attention. There are two oxids of hydrogen, two of carbon, five of nitrogen, and one of oxygen. Only one of the oxids of hydrogen, the monoxid, H_2O , is of great interest. It is needless to speak of the occurrence of water on the earth, or of most of its properties and uses, hence the treatment will be confined to those parts of special interest to the chemistry student.

226. History. — Cavendish, 1781, combined hydrogen and oxygen by an electric spark in a strong glass vessel. Humboldt and Gay Lussac, 1805, first showed that two volumes of hydrogen combine with one volume of oxygen to form water. Hydrogen dioxid was discovered by Thénard, 1818, but was known only in solution previous to 1890. Ozone was discovered by Schönbein, 1840.

CHEMISTRY OF WATER.

227. Preparation. — In the experiment of burning hydrogen it was found that the product was always water. In the decomposition of water by electrolysis (Fig. 84), we found there was twice as much

hydrogen as oxygen by volume, but only one-eighth as much by weight. In the synthesis of water by the eudiometer (Fig. 85), the same relations

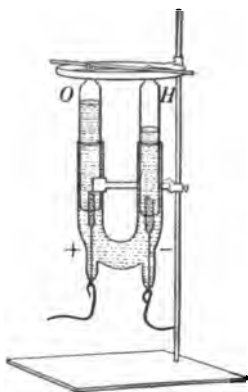


FIG. 84.

can be shown. A graduated tube is filled with mercury and inverted over a mercury bath. Hydrogen and oxygen are introduced, two volumes of the former (from the top to C) to one of the latter (from C to B). An electric spark causes the whole of the two gases to combine. If the water formed, and the hydrogen and oxygen

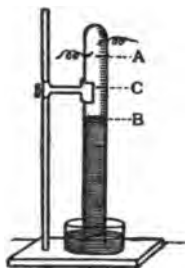


FIG. 85.

which entered into its composition are vaporized and at the same temperature, say 100° , the water vapor will occupy as much volume as the hydrogen alone, or two-thirds as much as the sum of the two gaseous factors, from which, by Avogadro's law, we obtain H_2O as the symbol of water. Water is formed whenever compounds of hydrogen, *e.g.*, hydrocarbons, are burned; and it is a very common product in chemical reactions, in double decompositions, and in dissociation by heat, etc., as in the preparation of N_2O , and the action of heat on sugar or oxalic acid.

228. Sources and Impurities. — Water as it occurs in and on the earth is probably never absolutely pure, but contains solutions of different substances, according to the kinds of soil or rock with which it has come in contact. Rain is the source of the land water, it having been taken up by evaporation from the ocean, lakes, and rivers, to be returned again. As it falls, a part flows off, as surface water, in brooks and rivers, a part sinks into the earth, slowly percolates through earth and rocks, and finally comes to the surface in springs and driven wells. Much water is absorbed from soils by the roots of plants, and

exhaled through their leaves into the atmosphere. It is estimated that on an acre of crops in Great Britain, from 3,000,000 to 5,000,000 pounds are annually exhaled from the leaves. The two sorts of water, from rivers and from springs, differ considerably in the character of their impurities.

River water contains organic matter, spring water generally holds salts in solution. Organic matter tinges water yellow, as can be best seen in many a waterfall. This organic material is either dead or living. Micro-organisms so minute that millions may exist in a cubic centimeter and be entirely invisible, are contained in all stagnant ponds and in much river water. Some of them are harmless, others are germs of infectious disease.

The salts in spring water are derived from the rocks and earth through which it has found its way. Chalybeate (pronounced kā-lib'e-ate) waters contain compounds of iron in solution. Sulfur springs contain H_2S , and water in limestone regions is hard and limy.

229. Hard Water contains either lime or magnesium salts in solution, usually the former. It is called *hard* by reason of its action on soap, which, instead of dissolving in the water, forming a lather, and cleansing the skin, combines with the salts to form an insoluble lime or magnesium soap, that appears as a precipitate, or a scum on the surface. Hard water is of two kinds — that of *temporary hardness*, and that of *permanent hardness*. The first has either CaCO_3 or MgCO_3 in solution; *i.e.*, it contains $\text{H}_2\text{Ca}(\text{CO}_3)_2$ or $\text{H}_2\text{Mg}(\text{CO}_3)_2$ (see Chap. XXI). Boiling expels CO_2 and thus precipitates the carbonates of Ca or Mg, which often appear as a crust on boilers and kettles.

The water is softened in that way. Permanently hard waters contain CaSO_4 or MgSO_4 , and can be softened by treatment with Na_2CO_3 .

230. In the Human Body.—Water constitutes about 60% of the human body, it being found in all the tissues. The enamel of the teeth contains least, 0.2%, the saliva about 99.5%. Every article of food contains some water, of which we take into the system some $2\frac{1}{2}$ liters each day, on the average. Plant life also contains a large proportion of water.

Exp. 124. — Dissolve, by boiling, a thin shaving of soap in 10 or 15^{cc} of soft or distilled water. When it is dissolved, note any froth or lather on shaking it. Prepare 10^{cc} of $\text{H}_2\text{Ca}(\text{CO}_3)_2$ solution (Chap. XXI), add 2 or 3^{cc} of the soap solution to it, and shake the tube well. See whether there is any permanent lather, or a precipitate. Add more soap solution, shake it, and observe again. Continue to add soap solution till the froth lasts several minutes.

Exp. 125. — Test, as above, a weak solution of MgSO_4 , then a strong solution, with the soap solution, and note which is more easily softened.

Exp. 126. — Prepare some $\text{H}_2\text{Ca}(\text{CO}_3)_2$, boil it, to expel all CO_2 , filter, then apply the soap test to the filtrate.

231. Properties. — Water exists in three states, solid, liquid, and vaporous. It freezes at 0° — suddenly expanding considerably as it passes into the solid state — and boils at 100° (under 760^{mm} pressure). If the pressure is greater, the boiling-point is raised (*i.e.*, it takes a higher temperature to overcome a greater pressure). Diminished pressure lowers the boiling-point. Salts dissolved in water raise its boiling-point and lower the freezing-point, to an extent depending on the kind and quantity of salt. Water evaporates at all temperatures, even from ice.

Pure water has scarcely any taste or smell, and in small quantities, no color. Water falling after a long rain is nearly pure. The solvent action and other properties of

this compound have been treated of previously. Salts dissolved in water undoubtedly form a weak chemical union with the water, but so weak as to be commonly regarded as a physical change merely.

232. Boiling-Point.—The boiling-point of water (or of any liquid) is the temperature at which its pressure as a vapor just begins to exceed the external pressure of the air, so that bubbles of steam formed within the liquid rise and pass into the atmosphere.

233. Filtration of water for drinking purposes does not remove the salts in solution, but only organic and other matter in suspension. Small charcoal or sand filters are of little utility in removing micro-organisms. The "Pasteur filter," or one made of natural stone, is the most serviceable. On a large scale, the water-supply of a city is now freed from germs by filtering it through several feet in thickness of sand and gravel, extending over some acres. After a day or two the water is diverted to another similar filter, the first being allowed to dry for an equal time. Filtering removes the germs, which appear to be destroyed by oxidation. Sewage is thus purified, and rendered colorless, odorless, free from bacteria, and harmless to drink.

234. Sea Water.—The ocean, it is thought, may contain all known elements, but not over half of them can be easily detected. The salts of sodium and magnesium are most abundant. The saline taste is due to NaCl , the bitter taste to MgSO_4 and MgCl_2 . A liter of sea water (about 1000g) contains over 37g—nearly 4%—of various salts, 29 of which—almost 3%—are NaCl . That iodine exists in sea water is known because certain seaweeds secrete it. Silver is sometimes found on the copper sheathing of ships, though analysis fails to show any silver in sea water. The total aggregate of gold in circulation in the waters of the ocean, is said to exceed that in circulation in all the countries of the earth, and the total amount of NaCl in the sea to be equivalent to a globe the size of the moon.

235. Distillation.—All sorts of water may be purified by distillation. The process consists in vaporizing it, and then cooling and condensing it again to a liquid.

Most of the impurities of water are less volatile than water itself, hence when the liquid is boiled, the salts, etc., in solution are left behind, and it is mainly pure water that is condensed. Substances which vaporize at a lower temperature than water, like alcohol or ammonia, would not be removed by distillation. The apparatus employed

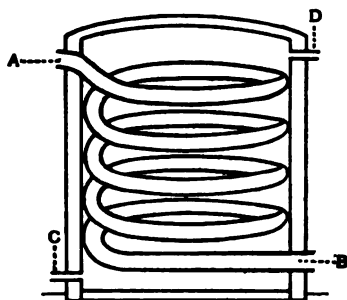


FIG. 86.

is known as a still, or a Liebig's condenser. In the still a coil or worm — made of block tin (*A*, *B*, Fig. 86) and surrounded by cold water entering at *C* and escaping at *D* — serves to condense the vapor, which runs out at *B*. In the condenser (Fig. 87) the same thing is effected with glass tubes. On evaporating a drop of distilled water on platinum foil there should be no residue left, but from ordinary water a slight trace of deposit is seen. Distilled water has a flat taste. For drinking purposes it may be aerated by passing purified air or CO_2 through it.

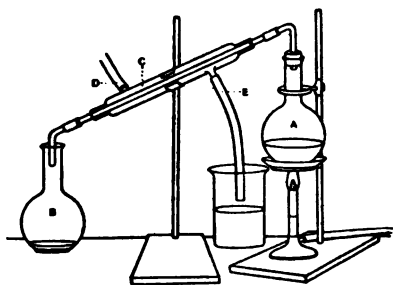


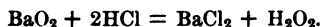
FIG. 87. — Liebig's condenser. *A*, water to be vaporized. *B*, distilled water. *C*, jacket for water which enters at *D*, escapes at *E*, and condenses the steam in inner tube.

Exp. 127. — Arrange a Liebig's condenser (Fig. 87), put some water

into the flask, boil it, collect the distillate, taste the latter, and evaporate a drop or two on platinum foil in a room free from dust. Test in the same way some undistilled water.

HYDROGEN DIOXID.

236. Preparation.—This compound occurs only in very small quantities in the atmosphere. It is prepared by acting on barium dioxid, BaO_2 , with a dilute acid, as HCl , H_2SO_4 (or with CO_2).



Exp. 128.—Pour on 1 or 2g of powdered barium dioxid, BaO_2 , just enough water to make a thin paste, then add 5 or 10cc of dilute HCl —enough to dissolve it to a clear solution. This forms a solution of H_2O_2 .

237. Properties.—Hydrogen dioxid, or peroxid, is a colorless, syrupy liquid, with a bitter and corrosive taste. It bleaches the skin white and is an exceedingly strong oxidizing agent, very unstable when pure, but readily soluble in water, though at first it sinks on mixing the two liquids. The dilute solution is more stable. It is strongly antiseptic. Like ozone it will even oxidize silver, and also set free iodine from KI , which forms a test for it. It forms with $\text{K}_2\text{Cr}_2\text{O}_7$ solution a blue liquid, best made visible by ether—a very delicate test for it.

Exp. 129.—To the solution of H_2O_2 add 2 or 3 drops of $\text{K}_2\text{Cr}_2\text{O}_7$ solution, then a little ether. Shake the whole. A blue liquid should appear, which is dissolved by ether and carried to the surface.

Exp. 130.—Pour a few drops of H_2O_2 into indigo solution and boil it. The color should disappear.

Exp. 131.—Add a drop or two to some water containing a very little starch and potassium iodide solution, $2\text{KI} + \text{H}_2\text{O}_2 = 2\text{KOH} + 2\text{I}$.

Uses.—It is used in surgery as an antiseptic, in the laboratory as an oxidizing agent, and by artists to renovate old oil paintings.

OZONE.

238. Ozone may be regarded as an oxid of oxygen, the molecule being O_3 or O_2O . It is simply an allotropic form of oxygen, chemically much more active than the ordinary form, and more unstable. Three

volumes of oxygen form two volumes of ozone, or $3\text{O}_2 = 2\text{O}_3$. Very small quantities of ozone, like H_2O_2 , are formed in the air, but in varying proportions. It is formed during thunderstorms by artificial electrical discharges. The quantity of ozone produced is very small, about 5% being the maximum artificially prepared, and the usual amount far less than that.

Ozone is a colorless gas, of disagreeable odor, and is a powerful oxidizing agent. It will change S, P, As, etc., into their *ic* acids in presence of water. Cotton cloth and linen were formerly bleached by spreading them on the grass and leaving them for weeks to be slowly acted on by H_2O_2 and ozone. The element is an antiseptic and disinfectant, and serves to clear the air of noxious gases and germs of infectious disease. Hence the air of cities contains less ozone than country air. When it breaks up, two volumes of ozone become again three of oxygen, but a third part of it may combine with the substance to be oxidized. $2\text{KI} + \widehat{\text{O}}_3 = \text{K}_2\text{O} + \text{I} + \widehat{\text{O}}_2$. The formation of ozone is attended by absorption of heat, hence it is endothermic. Its decomposition liberates heat. It may be tested by its peculiar odor and its action on iodo-starch paper, liberating iodine, which colors starch blue. It acts in this respect like chlorine.

Exp. 132. — Scrape off (under water) the outside coating from a stick of phosphorus and put the latter into a beaker. Half cover the phosphorus with water, and cover the beaker with glass. In a few minutes remove the cover, note the odor, and hold in the beaker a piece of moist iodo-starch paper.

CHAPTER XXI.

OXIDS OF CARBON.

CARBON DIOXID.

239. There is, perhaps, no gas more interesting, by reason of its history, its peculiar properties, its effect on animal and vegetable life, and its great abundance and wide diffusion, than carbon dioxid. It is the first gas that was ever carefully studied. Millions of tons of it are thrown into the air yearly by the combustion of compounds of carbon, the exhalations of animals, volcanic eruptions, and the reduction of carbonates. Large quantities of it are used as a beverage in mineral waters, and it is the great gaseous food of plants. It is of interest alike to the chemist, the geologist, and the sanitarian.

240. History.—Van Helmont, about 1600, observed that the gas obtained from burning wood, fermentation, or the action of an acid on limestone, differed from ordinary air, in that it would put out fires. He named it “wild gas.” In 1755 Black obtained it from carbonates of sodium and potassium, in which he said it was fixed, and named it “fixed air.” Lavoisier proved its composition, obtaining it by heating HgO mixed with C. Dalton, 1804, showed that the molecule consists of one atom of carbon united to two atoms of oxygen.

Names.—*Carbon dioxid*, carbonic acid, carbonic acid gas, carbonic anhydrid.

241. Occurrence.—Uncombined this gas exists in the air, of which it forms from .03% to .06%, the average

being about 4 parts in 10,000 of air. More is found in large cities than in the country or above the sea.

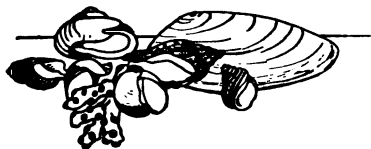
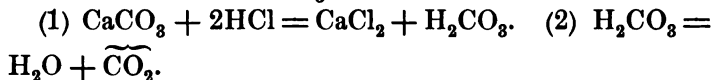


FIG. 88. — Shells and coral consisting of CaCO_3 .

It occurs combined in all carbonates, the most abundant of which is limestone, CaCO_3 . Oxalates, as CaC_2O_4 , also

are a source of it. The amount of CO_2 in our atmosphere has been computed at over six trillion pounds, more than would result from the combustion of all the vegetable and animal matter now on the earth. Molluscan shells, corals, and chalk are mainly carbonate of lime, CaCO_3 (Fig. 88).

242. Preparation and Formation.—The best way to prepare CO_2 is to act upon a carbonate with an acid. In general any acid, except H_2S and HCN , will act on any carbonate and liberate CO_2 . For laboratory purposes calcium carbonate, CaCO_3 , and HCl are most available.



Carbonic acid, H_2CO_3 , is probably the first product, but being very unstable, at once breaks up, as above. A high temperature will also decompose carbonates into CO_2 and the oxid of the metal. CaCO_3 begins to break up at a red heat. In this way lime, CaO , is made. Heat will also decompose oxalates, liberating CO_2 and CO , and leaving the metallic oxid, *e.g.*, $\text{CaC}_2\text{O}_4 = \text{CaO} + \widetilde{\text{CO}}_2 + \widetilde{\text{CO}}$. Carbon dioxid is also formed whenever carbon in any form burns with plenty of oxygen. $\text{C} + 2\widetilde{\text{O}} = \widetilde{\text{CO}}_2$. It is formed by all animals as a product of respiration, in the

decay of plants and animals, and in almost every kind of fermentation. Volcanic eruptions throw out great volumes of it into the air. It is the deadly "choke-damp" formed in mines by the explosion of mixtures of CH_4 , etc., with O . $\widetilde{\text{CH}}_4 + 4\widetilde{\text{O}} = \widetilde{\text{CO}}_2 + 2\text{H}_2\text{O}$.

Exp. 133.—Put into a gas generator 10 or 15 $\frac{1}{2}$ marble chips, CaCO_3 , cover them with water, and pour in small successive portions of HCl . The gas escapes and may be collected by downward displacement, as in Fig. 89. Ascertain when the receiver is full by thrusting a lighted splint into it. For a large quantity of the gas use a Kipp apparatus (Fig. 90). Keep the receivers covered, right side up.

Exp. 134.—Liberate some CO_2 , in the same way as above, from molluscan shells—oysters, clams, snails, etc.—or from coral or chalk. Test it by Exp. 139.

Exp. 135.—Hang a glass funnel over a burning candle to catch the CO_2 liberated, and collect it as in Fig. 91; then test it with lime water.

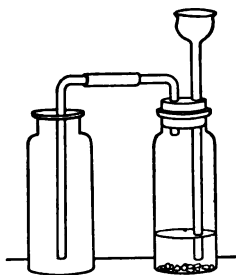


FIG. 89.

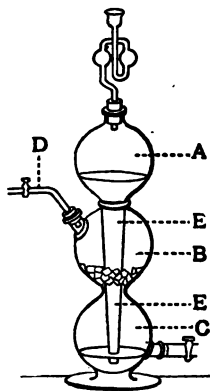


FIG. 90.

Exp. 136.—Heat some "plain soda"; or Apollinaris water may be boiled in a flask and the gas collected and tested.

243. Properties and Tests.— CO_2 is a heavy gas with no color, but with a pungent odor and sharp prickly taste. Being so heavy, it diffuses slowly, and often accumulates at the bottom of old wells. Before going into one of these, the gas should be tested with a lighted candle. If the flame is extinguished, there is danger. CO_2 is not a supporter of combustion

or of respiration. It cannot be breathed, because it ex-

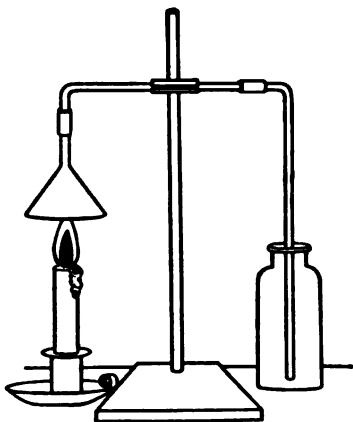
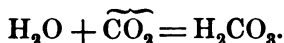


FIG. 91.

cludes oxygen and thus may cause death; but the old view that CO_2 is poisonous is not now held; in fact, when it is taken in soda-water and mineral waters, the effect on the system is beneficial. Distilled water tastes flat unless aerated by CO_2 . It is quite soluble in water, with which it seems to form the weak acid, H_2CO_3 .

Lime water, $\text{Ca}(\text{OH})_2$ solution, is used as a test for

CO_2 . Insoluble calcium carbonate, CaCO_3 , is formed, and at first precipitated. $\text{Ca}(\text{OH})_2 + \widetilde{\text{CO}_2} = \text{CaCO}_3 + \text{H}_2\text{O}$. If the CO_2 continues to pass into the lime water, all the lime finally combines, and the excess of CO_2 then unites with the H_2O , making H_2CO_3 .



This acid, H_2CO_3 , now reacts on the CaCO_3 , forming with it the bicarbonate of calcium, $\text{H}_2\text{Ca}(\text{CO}_3)_2$ (but not liberating CO_2). $\text{H}_2\text{CO}_3 + \text{CaCO}_3 = \text{H}_2\text{Ca}(\text{CO}_3)_2$.

The bicarbonate is soluble, and hence the precipitate dissolves and the liquid clears. The precipitate can be re-obtained by boiling, which drives out part of the CO_2 from the $\text{H}_2\text{Ca}(\text{CO}_3)_2$. $\text{H}_2\text{Ca}(\text{CO}_3)_2 = \text{CaCO}_3 + \text{H}_2\text{O} + \widetilde{\text{CO}_2}$. This paradoxical phenomenon is usually explained by saying that CaCO_3 is insoluble in pure water, but

soluble in water which has CO_2 . "Hard water" often contains $\text{H}_2\text{Ca}(\text{CO}_3)_2$ in solution. $\text{Ba}(\text{OH})_2$ solution is also a test for CO_2 , precipitating white BaCO_3 . CO_2 , when passed into any hydrate solution, forms the corresponding carbonate. This is exactly what we should expect, for CO_2 with H_2O is an acid, and hence with addition of a base or hydrate will form a salt. $2\text{NaOH} + \widetilde{\text{CO}_2} = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$.

Indirectly, lime water becomes a test for carbonates, for an acid liberates CO_2 from a carbonate, and this is tested by lime water. K or Na will burn in CO_2 with formation of K_2CO_3 or Na_2CO_3 and C. This gas, like others, can be frozen by cold and pressure.

244. Oxidation in the Human System.—Oxygen is taken into the lungs, and carbon dioxid and water are breathed out. In this process the O is reduced from about 21% to 16%, by volume. The exhalations also contain nitrogen, argon, and the surplus oxygen. About a quarter of the O has been consumed in heating the body and oxidizing its products, which are mainly compounds of C, H, O, N. At one time it was thought that this oxidation took place wholly at the lungs, but it is now known that the union of carbon, hydrogen, etc., with oxygen takes place in all the tissues and in all parts of the body, even on the surface. Oxygen is taken into the lungs, passes from there through the thin membrane into the blood, by reason of the attraction it has for hæmoglobin of the red corpuscles. With these corpuscles it forms a compound, oxy-hæmoglobin, and thus circulates to all parts of the system (Fig. 92). The oxy-hæmoglobin

parts with its oxygen wherever it finds compounds of

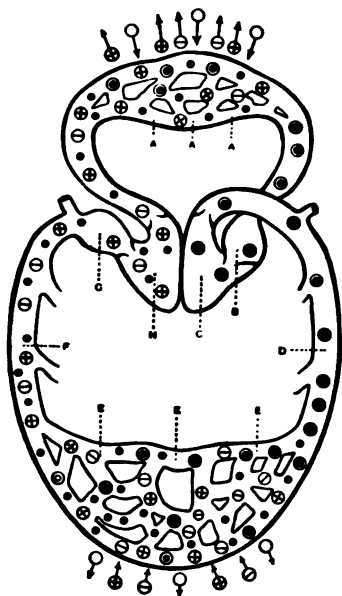


FIG. 92. — Blood circulates from *A* through *B, C, D, E, F, G, H* to *A*. *A*, capillary system of lungs; *B*, left auricle; *C*, left ventricle; *D*, arterial system; *E*, capillaries of body; *F*, venous system; *G*, right auricle; *H*, right ventricle; ●, hæmoglobin, or red blood corpuscles; ○, oxy-hæmoglobin, or corpuscles with oxygen; ○, oxygen; ⊙, water; ⊕, carbon dioxide; arrows show direction of movement of O , H_2O , CO_2 .

carbon, hydrogen, etc., ready to be oxidized, forming with them CO_2 and H_2O . The oxidation is mainly in the capillaries, where the corpuscles pass in "single file." The products are carried back through the veins to the lungs, whence they are exhaled. Arterial blood is much purer and of a redder color than is venous. The system is in this way purified, and the waste is supplied by the digestion and assimilation of food. The oxidation of food products, after assimilation, keeps up the heat of the body as really as the combustion of carbon or sulfur liberates heat. The average temperature in man is 37° ($98.6^\circ F.$). Any excess of heat produces perspiration, or is changed into other forms of energy. The maintenance

of temperature at nearly a fixed degree is necessary to health and life. But in disease the temperature of the body deviates to some extent from the normal. In

Asiatic cholera it is sometimes as low as 25° – 26° (77° – 79° F.), while in pneumonia it may rise to over 41° (106° – 107° F.). Considerably higher temperatures than these have been noted ; but if this condition is continued, the blood corpuscles are killed, and the person dies.

245. Deoxidation in Plants. — Since CO_2 is so constantly poured into the atmosphere, why is there not more CO_2 and less free oxygen in the air to-day than a thousand years ago? The answer may be found in the growth of vegetation. In the leaf of every plant are thousands of little chemical laboratories. A single tree often has acres of foliage surface exposed to sunlight and air; CO_2 , diffused in small quantities in the air, passes into the leaf, mainly from the under side through the stomata, or little mouths (Fig. 93). Within the leaf, probably in the green chlorophyll grains, it is decomposed by the radiant energy of the sun. The carbon is built into the woody fiber of the tree, and the oxygen is ready to be rebreathed or burned again. CO_2 contributes to the growth of plants, O to that of animals, and the constituents of the atmosphere vary but little from one age to another. The compensation of nature is here well shown. Plants feed upon what animals discard, transforming it into material for the sustenance of the latter, while



FIG. 93. — Partial vertical section of leaf much magnified, showing CO_2 entering stomata on under side of leaf, and O emerging. \oplus , CO_2 ; \odot , oxygen; \bullet , chlorophyll granules.

animals prepare food for plants. All the carbon in plants is supposed to come from the CO_2 in the atmosphere. Animals obtain their supply of carbon from plants. The utility of the small percentage of CO_2 in the air is thus seen. Fig. 94 illustrates the migration of a carbon atom, from the formation of CO_2 by the burning of fuel, *A*, to its fixation in food

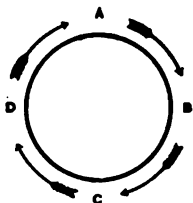


FIG. 94.

plants, *B*, thence in the tissues of animals which feed on these plants, *C*, and finally in the human being, *D*, who eats the meat of the animal, and then has his carbon oxidized and again thrown into the air. Such migration is not peculiar to carbon, but

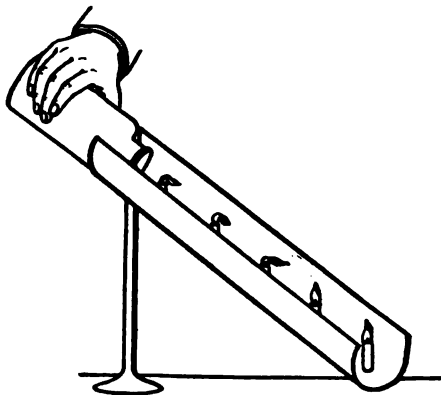


FIG. 95.

can be traced in any common element.

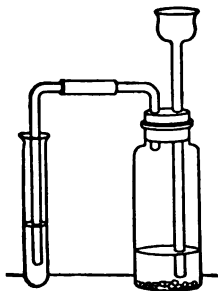


FIG. 96.

Exp. 137.—Try the odor of CO_2 . Thrust a glowing splint, then one well burning, into a receiver of CO_2 . Ignite a bit of sulfur or phosphorus and thrust it into a receiver of the gas. Pour some gas down over a candle flame. With a large quantity of CO_2 several flames can be extinguished and the gas poured down like a liquid, as in Fig. 95.

Exp. 138.—Pass some CO_2 from a generator into a solution of blue litmus (Fig. 96).

Exp. 139. — Let some CO_2 from a generator bubble into a test tube containing 10^{cc} of a solution of lime water. Note the immediate effect, and after it has continued for some time see whether the liquid clears. If so, boil it for a minute in the flame.

Exp. 140. — Repeat Exp. 139, using $\text{Ba}(\text{OH})_2$ solution in place of $\text{Ca}(\text{OH})_2$.

Exp. 141. — Insert one end of a small glass tube in the mouth, the other in a test tube of lime water, and blow into the latter for a minute.

Exp. 142. — In an open evaporating dish expose a little $\text{Ca}(\text{OH})_2$ solution for some time to the air of the room, then examine it for any precipitate. The per cent of CO_2 in the air of a room may be determined as follows, by Wol-

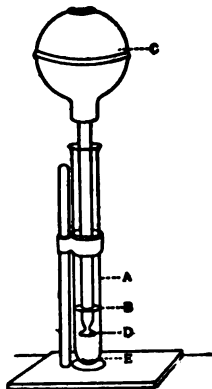


FIG. 97.

pert's apparatus (Fig. 97). Fill the rubber bulb *C* with air, and force carefully the contents through lime water, *B*, *E*, in the tube *A*, which contains a black mark, *E*, in the bottom. This mark is just concealed by a known weight of CaCO_3 . The capacity of *C* is known, and it is noted how many times the bulb must be filled to conceal the mark. From the data the per cent is computed.



FIG. 98.

Exp. 143. — Put a large beaker on one beam of a balance and counterpoise it. Then pour into the beaker some CO_2 gas (Fig. 98).

246. Uses. — Carbonic acid gas is used for making "soda water," and as a basis of mineral waters, in chemical engines as an extinguisher of fires in their early stages, in bread-making (causing the dough to rise by its formation), and it is employed very extensively in the alkali

manufacture, *e.g.*, Na_2CO_3 . In fire-engines H_2SO_4 in one cistern is let into another cistern containing Na_2CO_3 solution.

In nature the gas has important functions. By its solubility in water it renders insoluble carbonates soluble; it wears away and destroys rocks, being the only abundant acid found free, and forms carbonates, especially CaCO_3 , which is found in every part of the world.

CARBON MONOXID.

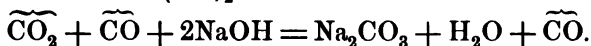
247. Only two oxids of carbon are known. Though the dioxid, CO_2 , is far more common, the monoxid, CO , occurs in large quantities in the gas by which our houses are lighted, and is formed in the reduction of iron ores, etc. The carbon is in this case only half saturated with oxygen, hence the compound is chemically very active and ready to combine with other elements like Cl , O , etc., with which it forms more stable gases. CO is very poisonous, and all experiments with it must be made with care.

248. History. — Lassone first discovered this gas, about 1776. Twenty years later Priestley obtained it, and named it “phlogisticated water.” Lavoisier supposed it to be hydrogen. Cruikshank, 1800, proved it an oxid of carbon.

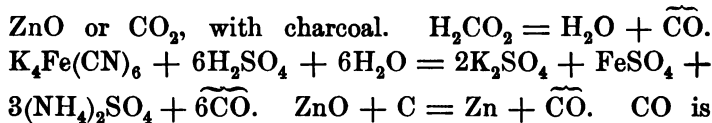
Names. — Carbon monoxid, carbon protoxid, carbonic oxid.

249. Occurrence. — Probably the gas does not occur naturally anywhere except as a product of half-combustion in furnaces, coal fires, and slightly in gas-lights, smouldering coal, etc. Oxalic acid and oxalates are the main compounds from which it is obtained. Formic acid, H_2CO_2 , also gives it.

250. Preparation. — One way of preparing this gas is to act upon oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, with sulfuric acid, H_2SO_4 , and heat. It will be seen that $\text{H}_2\text{C}_2\text{O}_4$, which is a solid, consists of H, C, and O in the exact proportion to form H_2O , CO_2 , CO. Heat alone will break up the acid into these constituents, but H_2SO_4 aids in the operation, and also absorbs the H_2O , leaving the two gases CO_2 and CO completely intermingled. Remembering the affinity which CO_2 has for soluble hydrates, we can separate it by passing the mixture into a solution of sodium hydrate, NaOH , or hydrate of potassium, KOH , or of calcium, $\text{Ca}(\text{OH})_2$.



The CO, being insoluble in H_2O , can be collected like hydrogen. The gas can also be prepared by the action of H_2SO_4 on either formic acid, H_2CO_2 , or potassium ferrocyanid, K_4FeCy_6 , or by heating certain oxids, as



CO is formed and plays a very important rôle in the iron reduction furnace, and makes up from a quarter to a third of the constituents of "water gas."

Exp. 144. — Put into a small flask 10s of oxalic acid crystals, $\text{H}_2\text{C}_2\text{O}_4$, and cover it well with H_2SO_4 . Arrange and connect the apparatus as in Fig. 99, having the delivery tube from the flask extend

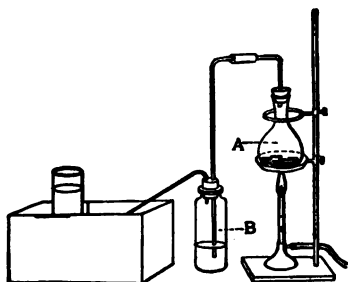


FIG. 99.

into some NaOH solution. Collect the escaping gas over water, and avoid inhaling any. Heat the flask slowly, and do not allow the gas to escape into the air, but keep it over water till wanted in the next experiment.

251. Water Gas.—This is so called because made from water. It constitutes the basis of the illuminating gas used in many large cities at the present time. Steam (superheated) is passed over red hot carbon (anthracite coal) when this reaction occurs.

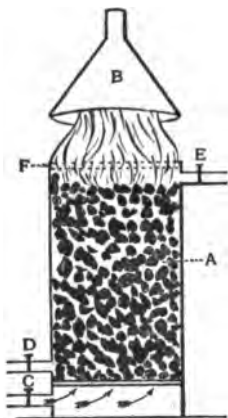
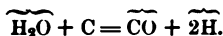


FIG. 100.

The coal contained in large cylinders (Fig. 100, A) is first set on fire, air passing in at C, and CO_2 and CO being formed. The top of the cylinder is opened at F, and the escaping CO burns with a vivid blue flame to CO_2 , which passes off by the hood B. This process is continued till the coal is thoroughly burning, when the air draught C, and the top of the cylinder F, are closed, a valve, D, from the steam generator is opened, and also the valve to a discharge pipe, E. Steam is forced in at D, and the products CO and H pass out at E to a reservoir. After a few minutes it is necessary to turn off the

steam and re-heat the coal, as at first. As both CO and H burn with a feeble blue light, it is necessary to "enrich" the gas, i.e., mix with it a small percentage of light-giving constituents. For this, petroleum or naphtha is destructively distilled, and the products (hydrocarbons that are rich in carbon) are mingled with the H and CO, and serve as the light-giving constituents.

252. Properties.—*Physical.* Carbonic oxid is a gas, colorless and with no taste, having a slight characteristic odor. It is very poisonous, being the deadly constituent in illuminating gas. It unites with the hæmoglobin of the blood to the exclusion of oxygen, and a small percentage of it has proved fatal.

Chemical. It is a compound in which the affinity of carbon is but half satisfied, hence the readiness with

which it combines with more oxygen. It burns with a lambent blue flame, forming CO_2 . This constitutes a test.

$\widetilde{\text{CO}} + \widetilde{\text{O}} = \widetilde{\text{CO}_2}$. Oxalates are tested in this way. It also unites with chlorin to form COCl_2 , carbonyl chlorid. It is not a supporter of ordinary combustion. At high temperatures where oxygen is wanting but CO_2 is present, red-hot carbon robs the CO_2 of half its oxygen.

$\widetilde{\text{CO}_2} + \text{C} = 2\widetilde{\text{CO}}$. CO_2 then becomes an oxidizing agent.

CO is often a reducing agent, as in the iron furnace, where it combines with the oxygen of the ore and leaves iron. $\text{Fe}_3\text{O}_4 + 4\widetilde{\text{CO}} = 3\text{Fe} + 4\widetilde{\text{CO}_2}$.

Exp. 145.—Having removed from the water a receiver of the gas CO (Exp. 144), thrust a lighted splint into it. Retain in the receiver a part of the product of combustion, and finally shake up a little lime water with it. Try the action of lime water on CO gas. Unless all CO_2 is absorbed by NaOH solution, a precipitate will be obtained.

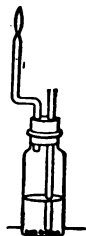


FIG. 101.

Exp. 146.—This must be done at the hood, and great care taken not

to let the gas escape, except through a flue. Make a philosopher's lamp as in Fig. 101, and connect it with the CO generator. When the air is expelled (test it as H was tested), light the gas. Collect some of the product of combustion in an inverted receiver and test it for CO_2 .

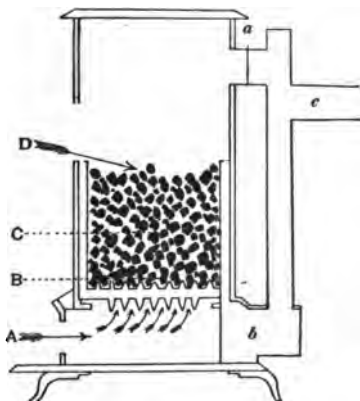


FIG. 102.

Exp. 147.—Collect over water a receiver two-thirds full of CO and the rest of O , and explode the mixture. For explosions never use anything but a wide-mouth receiver.

253. CO_2 and CO in a Coal Stove.—The fact that CO_2 is formed with abundance of oxygen,

and CO with a limited amount, is well shown in a coal fire (Fig. 102). Air carrying plenty of oxygen enters through the draught *A*, and CO_2 is first formed, *B*. $\text{C} + 2\text{O} = \text{CO}_2$. But as this rises to the middle of the hot coal *C*, where oxygen is wanting, it gives half its O to the carbon and becomes reduced to CO. $\text{CO}_2 + \text{C} = 2\text{CO}$. Reaching the surface, however, *D*, where there is plenty of oxygen, the CO becomes CO_2 , burning with a blue flame. $\text{CO} + \text{O} = \text{CO}_2$. The danger from having the back draft *a*, closed when the stove door is open, arises from the unburned CO being forced into the room to be breathed by the occupants.

254. Uses.—CO is a diluent in water gas, and a reducing agent in ore reductions, particularly iron. It forms a few compounds, like carbonyl chlorid and $\text{Ni}(\text{CO})_4$, nickel carbonyl.

CHAPTER XXII.

OXIDS OF NITROGEN.

255. While but two oxids of carbon and two of hydrogen are known, there are five well-marked compounds of nitrogen and oxygen. These are interesting not only individually, but because they form a series in which the ratio of oxygen to nitrogen increases regularly from the smallest quantity in which oxygen unites with any element up to five times that amount. Another curious fact is that they are not made by the direct union of N and O, as CO_2 , H_2O , SO_2 , P_2O_5 , etc. are, but are derived from nitrates and nitrites, either by the action of heat or of some reducing agent, such as the metals.

256. Names and Symbols.

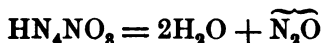
<i>Chemical Names.</i>	<i>Common Names.</i>	<i>Symbols.</i>
1. Nitrogen protoxid	nitrous oxid	N_2O
2. " dioxid	nitric "	N_2O_2 or NO
3. " trioxid	nitrous anhydrid	N_2O_3
4. " tetroxid	nitrogen peroxid	N_2O_4 or NO_2
5. " pentoxid	nitric anhydrid	N_2O_5

NO is the correct symbol of the dioxid, as shown by its vapor density (Chap. XXVII), and NO_2 for the gaseous tetroxid; but when the latter is liquefied, N_2O_4 may represent its molecule. None of these compounds are found free in nature.

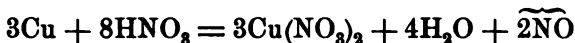
257. Preparation. — All the oxids of nitrogen may be made from nitrates (including HNO_3). Heat alone breaks

up nitrates, forming usually NO_2 (or N_2O_3) and O , and sometimes other oxids. Ammonium nitrate, NH_4NO_3 , on being heated gives the monoxid N_2O . Metals with HNO_3 usually give NO , N_2O_3 , or NO_2 . Which oxid is formed depends upon the temperature employed, the strength of acid used, and the metal which acts as a reducing agent. Concentrated acid or a high temperature tends to give the higher oxids.

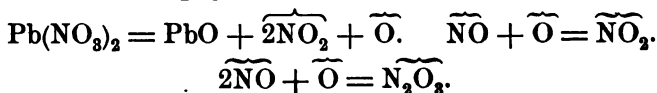
1. **Nitrogen monoxid**, N_2O , is made by heating ammonium nitrate, NH_4NO_3 , and collecting the dissociated gas over water.



2. **Nitrogen dioxid**, NO , is commonly prepared by acting on nitric acid with copper, though many other metals act similarly.



3, 4. The **trioxid**, N_2O_3 , and **tetroxid**, NO_2 , are products from breaking up nitrates and nitrites by the application of heat, or heat and sulfuric acid. They are also formed by the action of certain metals, as Sn , on HNO_3 . When NO is exposed to the air it at once unites with half its volume of oxygen and forms NO_2 , or with a fourth to form N_2O_3 .



5. The **pentoxid**, N_2O_5 , forms on heating phosphorus pentoxid, P_2O_5 , with HNO_3 , or on acting upon AgNO_3 with Cl .

Exp. 148. — Into a small flask put 10 or 15 $\frac{1}{2}$ of ammonium nitrate, NH_4NO_3 , and connect the apparatus represented in Fig. 103 to a pneumatic trough, having an intervening empty bottle to collect any liquid. Heat the flask. The salt will first melt, then partially decompose and vaporize, and N_2O should collect over water. This gas should not be inhaled, as it is likely to contain some undecomposed NH_4NO_3 , as well as some of the higher oxids of nitrogen.

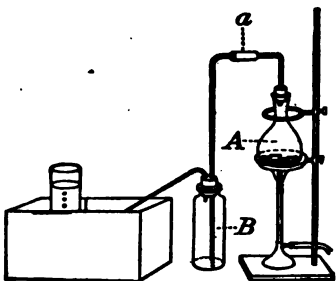


FIG. 103.

Exp. 149. — The gas generator (Fig. 104) has put into it 5 or 10 $\frac{1}{2}$ of copper filings. These are covered with water, and HNO_3 is added in quantity sufficient to make vigorous action. The escaping NO is collected over water.

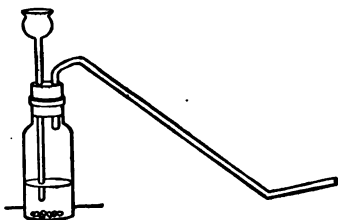


FIG. 104.

Exp. 151. — Heat in a test tube a few crystals of lead nitrate, $\text{Pb}(\text{NO}_3)_2$. One of the products is NO_2 . Thrust a glowing splint into the tube and determine another product (Fig. 105).

Exp. 152. — To a very little powdered starch add a few drops of HNO_3 , and heat the test tube containing the substances. The red fumes contain a mixture of N_2O_3 and NO_2 .

Exp. 153. — Pour a very little HNO_3 on some granulated tin in a test tube.

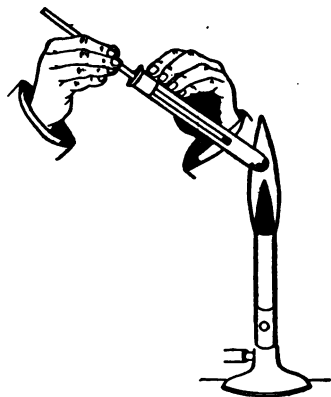


FIG. 105.

258. Properties. — Some of the leading properties of these oxids may be stated as follows :

N_2O , colorless gas. Sweet taste. Produces anesthesia. Supporter of combustion.

NO , colorless gas. Combines with O to form N_2O_3 and NO_2 . Supports combustion of P .

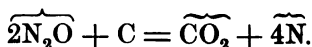
N_2O_3 , red-brown gas. Reduced to NO by H_2SO_3 , etc. With H_2O forms HNO_2 and HNO_3 .

NO_2 , red-brown gas. Reduced to NO by H_2SO_3 , etc. With H_2O forms HNO_2 and HNO_3 .

N_2O_5 , white, crystalline solid. Easily breaks up into NO_2 and O . With H_2O forms HNO_3 .

259. Nitrous Oxid, N_2O , is a gas without color, but with a slightly sweet taste and agreeable odor. When mixed with about one-fourth of its volume of oxygen, it produces intoxication and laughter ; hence its name *laughing-gas*, abbreviated by dentists to *gas*. As used in dental surgery it is unmixed with oxygen. Its physiological effect is then to produce temporary insensibility to pain. It will support respiration longer than any other gas except air and oxygen, but like other anesthetics it is liable to produce death from suffocation — or exclusion of oxygen — if administered too long. Most animals die quickly from inhaling it pure.

N_2O is soluble in its own volume of liquid H_2O . It liquefies under a pressure of 30 atmospheres. It will support the combustion of carbon more readily than the air will, but not so readily as pure oxygen. The product of combustion is CO_2 , N being set free.



Sulfur will burn in N_2O if strongly heated at first, but not otherwise, forming SO_2 . Phosphorus also burns in the gas and forms P_2O_5 .

260. Nitric Oxid, NO .— This is a colorless gas, only slightly soluble in water. Its taste and odor cannot be determined, as it combines at once with oxygen on coming in contact with the latter and forms NO_2 and N_2O_3 , and it is the taste and odor of these which the individual experiences as disagreeable and suffocating. NO is not a supporter of ordinary combustion, but phosphorus, if vigorously burning at first, continues to burn in it, forming P_2O_5 and liberating nitrogen. Potassium and sodium also burn in it, as well as other metals, *e.g.*, Fe and Zn, partially, and even C under certain conditions. The N and O are more strongly united in NO than in any of the other nitrogen oxids. Neither is NO a combustible gas, as hydrogen is, for though it unites vigorously with oxygen as soon as the two are mixed, the union is not attended with light, though considerable heat is liberated. The change is at once made evident by red-brown fumes of N_2O_3 and NO_2 appearing in place of colorless NO . In the sulfuric acid experiment it was called a carrier of oxygen.

261. The Trioxid, N_2O_3 , and Peroxid, NO_2 , are red-brown gases, indistinguishable from each other except by volumetric analysis, their chemical characters being nearly identical. They are very suffocating, intensely poisonous, and strong oxidizing agents, as illustrated in the H_2SO_4 manufacture, being reduced in the process to NO or forming $HNOSO_4$, by action of much water.

262. Nitrogen Pentoxid, N_2O_5 , is a white, crystalline, unstable solid, and has great affinity for water, with which it forms nitric acid. It is unimportant, for the acid is made by a more practicable process. .

Exp. 154. — Thrust a lighted splint into a receiver of N_2O . Try also a glowing splint, as with oxygen. See how the combustion compares with that in air and in oxygen. Test the product with lime water. Sulphur and phosphorus may also be tried.

Exp. 155. — Try the same experiment as above with a receiver of NO gas. Try it especially with phosphorus that is burning vigorously. Note the two colors of products left in the receiver, and see whether either subsides on standing.

Exp. 156. — Test a receiver of NO_2 as regards its action towards combustion.

Exp. 157. — Pass some N_2O from a generator into a receiver of NO over water. Also pass some O from a generator into a receiver of NO over water. N_2O will not redden the NO (if both are free from air), whereas O will. What two gases does this distinguish?

263. Uses. — *Nitrous oxid, N_2O ,* is used mainly by dentists in extracting teeth. It is liquefied and put up in metallic cylinders. On partially releasing the pressure by turning a valve a portion is vaporized, and this is inhaled. The next three oxids are of great service in the manufacture of sulfuric acid.

CHAPTER XXIII.

THE ATMOSPHERE

264. We live at the bottom of an ocean of gases called the atmosphere. What is the depth of that ocean, the distance to its surface, or whether it has a definite surface, we do not know. Formerly it was supposed that the atmosphere extended not over 50 miles from the earth's surface, but of late it has been held that it may extend through space to other planets, that particles of oxygen, water, and carbon dioxid pass by diffusion from the earth to Mars and other planets, and from them back to the earth. If there is a cosmical circulation of this kind, the air at great distances from the earth must be exceedingly attenuated.

265. History.—Air was one of the four elements of the ancients, the other three being earth, water, and fire. To the old philosophers any gas was air, as any thin liquid was water. The atmosphere was regarded as an element up to the time when Priestley discovered oxygen and Lavoisier explained its significance. Lavoisier was the first to obtain a quantitative analysis of the air with anything like exactness. This he did by burning out the oxygen with mercury heated for a long time. Argon, which makes nearly one per cent of the air, was not discovered till 1894.

266. Constituents.—The five main constituents of the atmosphere, or air, are nitrogen, oxygen, argon, water, and carbon dioxid. The first three may be called permanent constituents, as their proportion is quite constant,

varying only slightly. The water in the air is very variable in quantity. Desert winds are sometimes not more than one-fifteenth saturated. During rainy seasons the atmosphere is almost constantly at the saturation or dew-point. Warm air will hold more water than cold. Ordinarily on a pleasant day the atmosphere is within 66% to 70% of saturation. Having 100%, or all it can hold, air is said to be saturated, or at the dew-point. On cooling it, when at the dew-point at any temperature, precipitation — rain or snow — takes place. To show the presence of water in air, place a pitcher of ice-water in a warm room. The air on the outside of the pitcher is cooled to the dew-point and deposits part of its moisture.

Carbon dioxid, CO_2 , does not make up more than 3 or 4 parts in 10,000 of the air, *i.e.*, .03 or .04 per cent, on the average. Over cities the percentage is larger, above the ocean it is smaller. In crowded rooms and theatres the amount may run as high as .2 or .3 per cent. The total amount of CO_2 in the air is very great, 5000 billion tons it has been estimated, or enough to keep a forest which would cover the whole earth, land and water, growing for 8 years, or ordinary crops for 22 years. Lime water will show the presence of CO_2 in the air. The per cent can be roughly obtained by Wolpert's apparatus (Fig. 106 and Chap. XXI).

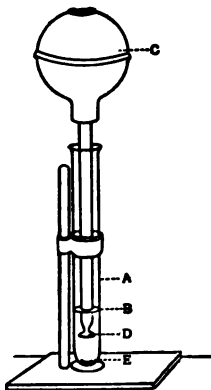


FIG. 106.

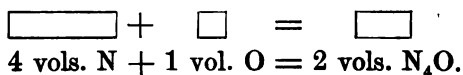
267. Air a Mixture of Gases.—That the air is a mixture of gases, not a compound of them, has been

already inferred. Water and CO_2 are too variable in quantity to enter into the discussion. But the following considerations show that nitrogen and oxygen also exist in the air as separate elements, and not as a compound.

1. *The proportion is variable.* The proportion of oxygen to nitrogen in the air varies but little, still it is not constant, as must be the case in a compound. The extreme limit for oxygen by volume is from 20.908% to 20.999%. Exactly 20% by volume of oxygen to 80% of nitrogen might indicate a compound with a symbol N_4O .

2. *They dissolve as elements.* If a compound with the symbol N_4O dissolved in water, it is evident that four times as much of nitrogen by volume must dissolve as of oxygen. The two elements could not dissolve separately, unless decomposed by the water. They do not, however, dissolve in the proportion 4 volumes to 1, but rather 1.87 to 1, when air is passed into water. This is determined by expelling the dissolved gases and analyzing them.

3. *They mix without heat or condensation.* If 4 volumes of nitrogen are mixed with 1 volume of oxygen, the mixture behaves very much like atmospheric air, but no heat is either liberated or absorbed, nor is there any condensation, as would be the case in a chemical union of the two gases. The vapor density of this mixture would be the same as that of the atmosphere, *viz.*, about 14.4, instead of 36, as would be the case if it were N_4O . $(14 \times 4 + 16) \div 5 = 14.4$. $(14 \times 4 + 16) \div 2 = 36$. Or, by volume, if a compound, N_4O , were formed, as a product of the mixture, the result would be as follows:



As only a mixture results, the volumes are :



4 vols. N + 1 vol. O = 5 vols. of mixture.

For further explanation of the vapor density see Chap. XXVII. From the previously supposed percentage of nitrogen in the air about 1% must be deducted for the newly found element argon.

268. Argon. — This new element was discovered in air, in the year 1894, by Rayleigh and Ramsay. Rayleigh found that nitrogen obtained from the atmosphere was $\frac{1}{4}\%$ heavier than if extracted from chemical compounds. From this it was believed there was another unknown constituent of the atmosphere. This was finally isolated in two ways. (1) A confined portion of air was submitted to a long series of electric sparks, which caused the oxygen and nitrogen to unite and form nitrogen oxids, oxygen being admitted as required to use up all the N. It was found that about 1% of the supposed N (or $\frac{1}{110}$ of the air) would not combine. Cavendish, more than a century before, had found the same thing, but did not follow up his discovery. Many successive experiments were made, and finally a quantity of the new, inert gas was obtained. In all cases there was found the same proportion of the residue uncombined. (2) Water and CO_2 were taken out of the air, then oxygen was removed by passing it over red-hot copper, and the nitrogen by passing it over red-hot magnesium turnings, with which it combined. To remove the last part of the N is a slow operation, requiring some two days, but it leaves pure argon. Obtained by either process, (1) argon is two and a half times as soluble in H_2O as nitrogen is, (2) its vapor density is 20 and molecular weight 40, (3) its spectrum is entirely distinct from nitrogen, (4) it liquefies at -121° with pressure of 50.6 atmospheres, and freezes at -191° , (5) it is the most inert of elements, no other substance being found with which it will combine, (6) its molecules seem to be monatomic. The name argon means inert substance. There is no simple test by which argon can be detected.

269. Other Constituents. — Other substances are often found in the atmosphere in minute and varying proportions, *e.g.*, ammonia may

constitute about one-millionth. Nitrites, nitrates, hydrogen dioxid, and ozone are often found in almost infinitesimal quantities, while the air of cities is impregnated with unburned carbon, dust particles, living and dead germs, etc. These are for the most part confined to the portion near the earth's surface. In pestilential regions the germs of disease sometimes contaminate the air for miles around.

WEIGHT OF GASES IN THE ATMOSPHERE.

Nitrogen	3,994,593 billion tohs.		
Oxygen	1,233,010	"	"
Carbon dioxid	5,287	"	"
Water vapor	54,450	"	"

CHAPTER XXIV.

LAWS OF COMBINATION.

270. General Law of Combination.— *An element always unites with other elements either in its least combining weight, or in some simple multiple of that weight. A gaseous element always unites either in its least combining volume, or in some simple multiple of it.*

This law is best understood when considered under four heads, *viz.*, (1) Law of Definite Weight, (2) Law of Definite Volume (for gases only), (3) Law of Multiple Weight, (4) Law of Multiple Volume (for gases only).

271. Law of Definite Weight.— *Any given chemical compound always contains the same elements in the same ratio by weight.*

The compound copper sulfid always contains copper and sulfur, and always has the same relative quantities of the two elements, *viz.*, 63 parts of copper by weight to 32 of sulfur. As 63 is the atomic weight of copper, and 32 is of sulfur, the symbol of the molecule of copper sulfid is CuS . Chlorate of potassium always contains potassium, chlorine, and oxygen, and in the proportion 39 of K, 35 of Cl, 48 of O by weight. The atomic weights, page 16, show why the symbol of its molecule is KClO_3 . In the same way all well-marked chemical compounds are unvarying in composition. One-ninth of the weight of water is hydrogen and eight-ninths oxygen. If water

were at different times composed of different elements in varying proportions, it is evident that no symbol for it would be possible. *A symbol means fixedness of composition.* Select several symbols and show how they illustrate the law.

Chemical attraction or affinity takes care of this ratio. If too much copper is used with the sulfur, it does not all combine; so with too much sulfur. When we pour HCl on Zn, if there is an excess of Zn, only just enough of it combines to satisfy the affinity for the acid, *viz.*, 65 of Zn to 70 of Cl. Sometimes, if there is too little of an element to form a given compound, another compound having different proportions of the elements will form. Burning in an abundant supply of oxygen, C forms CO_2 ; in a limited supply it often forms CO, containing half as much oxygen. As long as a given compound is formed, the relative weights of the elements remain perfectly constant. The proportion changes only on the formation of new compounds. When NO changes to NO_2 by the assumption of more oxygen, the ratio of nitrogen to oxygen changes from 14:16 in the first case to 14:32 in the second. The smallest particles undergo the same change, and hence the equation $\widetilde{\text{NO}} + \widetilde{\text{O}} = \widetilde{\text{NO}_2}$. When the dioxid of carbon is reduced to the protoxid by hot carbon, the ratio (or proportion) of the two elements is changed from 12:32 to 12:16, according to $\widetilde{\text{CO}_2} + \text{C} = 2\widetilde{\text{CO}}$.

272. Law of Definite Volume.—*Any given chemical compound which is made up of gaseous elements, always has the same elements in the same volumetric ratio.*

Ammonia is always composed of 3 volumes of hydrogen to each volume of nitrogen. According to this law a liter of hydrogen always combines with a liter of chlorine to form hydrogen chlorid. If 1 liter of chlorine were mixed with 3 liters of hydrogen, only $\frac{1}{3}$ of the latter would unite, the other $\frac{2}{3}$ remaining uncombined. If 2 volumes of O were put with 3 volumes of H, it is evident that all of both cannot enter into combination. Two volumes of O would require 4 of H, whereas 3 of H would require $1\frac{1}{2}$ of O, and $\frac{1}{2}$ volume of O would be left over. Nitrogen monoxid, if decomposed into its elements, would give 2 volumes of N to 1 volume of O ; hence the symbol N_2O . This law applies to all well-marked compounds that are made up of gaseous elements. It is evident that it cannot apply to solids and liquids, unless they can be vaporized and made to combine in that state. Iodin is a solid at usual temperatures, but it can be vaporized at a higher temperature, and then it is found that a cubic centimeter of the vapor combines with a cubic centimeter of hydrogen at the same degree of heat to form hydrogen iodid. So, too, the liquid Br, when vaporized, unites volume for volume with hydrogen to form hydrobromic acid, whose molecule is HBr.

On the other hand, the law does not apply to compounds of an element like Pb, which has not been vaporized. *The law of Definite Volume applies only to gases or elements capable of being vaporized.* Show how the law is illustrated by the symbols NO_2 , H_2O_2 , H_2S , SO_2 .

273. Law of Multiple Weight. — *In compounds made up of the same elements, one at least of the elements has a different relative weight in each compound, and this weight*

is always a simple multiple of its least combining (or atomic) weight.

There are two compounds of carbon and oxygen. In one the proportion of carbon to oxygen by weight is as 12 : 16, in the other as 12 : 32. The weight of oxygen in the second case is a simple multiple of that in the first. The least combining weight (atomic weight) of oxygen is 16, and 32 is a multiple of 16. The weight of carbon is the same in both compounds, and the molecular symbols are therefore CO and CO₂, called respectively carbon monoxid and carbon dioxid. Iron and sulfur combine in the two proportions by weight, 56 of Fe to 32 of S, and 56 of Fe to 64 of S. From the atomic weight of each element write symbols for the compounds, and show that the proportion of S illustrates the law. In a similar way analyze the symbols KNO₂ and KNO₃, MnO₂ and Mn₃O₄.

274. Law of Multiple Volume. — *In compounds made up of the same gaseous elements, one at least of the elements has a different volume in each compound, and this volume is a simple multiple of its least combining volume (usually atomic volume).*

Hydrogen and oxygen are gases, and they have two compounds. In one the ratio of H to O by volume is 2 : 1, in the other it is 2 : 2 ; i.e., there is twice as much O in the latter compound as in the former, while the H is the same in both. The symbols of these two compounds are H₂O and H₂O₂. The smallest combining volume of oxygen is, of course, 1, and the other compounds contain it in a multiple of this. If 2 volumes of H united with 2½ volumes of O, then the symbol would be H₂O_{2½} and the law of simple multiple proportion would

not hold. In the two oxids of phosphorus the O in the one case is 8 times, in the other it is 5 times its smallest combining volume, and the symbols are P_2O_8 and P_2O_5 .

This law, like the one of Definite Volume, is applicable only to such compounds as are made up of gaseous elements, since solids and liquids do not have the same volumetric relation.

275. Application. — Any single compound symbol illustrates the first law, any symbol whose elements are gases illustrates the second, any two or more symbols of the same elements in different proportions the third, and two or more symbols of the same gaseous elements in different proportions the fourth.

There are five known compounds of oxygen and nitrogen, which well illustrate the last two laws.

	NITROGEN BY WEIGHT.	OXYGEN BY WEIGHT.	NITROGEN BY VOLUME.	OXYGEN BY VOLUME.	SYMBOLS.
First oxid	28	16	2	1	N_2O
Second oxid	28	32	2	2	N_2O_2
Third oxid	28	48	2	3	N_2O_3
Fourth oxid	28	64	2	4	N_2O_4
Fifth oxid	28	80	2	5	N_2O_5

The proportion of nitrogen in each compound is unvarying, both in weight and volume, while the oxygen is in a multiple of its atomic weight, and also of its least combining volume. These multiples are respectively 1, 2, 3, 4, 5. In all the known compounds of oxygen there is a smallest combining proportion by weight and by volume. *The smallest weight is called its atomic weight, and the smallest volume its atomic volume.* The atomic volume is the volume equivalent to that of the hydrogen atom. In elements which have more than two atoms per molecule, e.g., As, the atomic volume is not the smallest volume. These laws furnish the main reason for supposing that the atom is indivisible, since all combinations are in multiples of the least combining weight and volume.

How many and which of the four laws are illustrated by these: $HgCl_2$? $HgCl_2$ and $HgCl$? N_2O and N_2O_3 ? $AgBr$? $Cu(NO_3)_2$? $CuCl$ and $CuCl_2$? H_2O and H_2O_2 ?

276. Limitations. — These laws, like all others, have their limitations. Take the first one, for example. It is said to hold in all cases of well-marked chemical compounds. But there are cases on the border line of chemistry and physics, and in these the law does not apply in its entirety. If we dissolve a small quantity of sugar in water, every part of the water becomes sweet ; if we increase the quantity of sugar to the point of saturation, it is sweeter than before ; but the Law of Definite Weight does not hold, for every part of the water has taken some of the sugar. This is where a physical solution differs from a chemical. Again, if we pass SO_2 gas into water, a very small but indefinite quantity will acidify the water, or we may add much more SO_2 . Thus the Law of Definite Weight does not prevail here, and it is often said that though a loose chemical union is formed, sulfurous acid, H_2SO_3 , does not exist as a definite compound. The same is true of the gas HCl . In a liter of water may be dissolved a fraction of a liter of the gas, or any quantity up to some 400 or 500 liters. In each case the whole is acid. Many other gases dissolved in water give indefinite mixtures, *e.g.*, CO_2 . Such solutions are regarded by some chemists as made up of definite chemical compounds dissolved in excess of the solvent water. Others regard them as simply physical solutions of the gases in water. Metallic alloys and amalgams, where an indefinite quantity of one metal dissolves in an indefinite quantity of another and forms a weak compound, are outside the Law of Definite Weight. When substances unite in other than exact proportions, the products are said to be mechanical mixtures or solutions of one in the other, and are not true chemical compounds. In all well-marked chemical compounds these laws hold good. Without them it is difficult to see how any science of chemistry would be possible.

CHAPTER XXV.

THE PERIODIC LAW.

277. Chemistry as a science dates from the time of Lavoisier, but until the discovery of the *Periodic Law* it was a science of fragments, without a satisfactory basis for a logical classification of the elements. A few elements, like the halogens, had been grouped together, as they showed similar or varying properties; but most of them stood alone, with no apparent connection. The *Periodic Law* has made a more connected science of chemistry. Each element is found to have a certain relation to others, and by this law unknown elements and their leading properties have been predicted, and afterwards discovered.

278. History. — Newlands, 1864, arranged the elements in octaves according to their atomic weights, but the classification was imperfect. Lothar Meyer and Mendelejeff, 1869-70, reclassified them, and announced the Periodic Law.

279. Periodic Law. — *The properties of elements are periodic functions of their atomic weights.*

According to the law, the properties of an element depend upon its least combining weight, and the elements can be divided into groups (or periods), the members of a given group resembling each other more than they resemble members of other groups.

If we place a few of the known elements in the order of their atomic weights, beginning with the smallest, and giving the nearest integral numbers, we have an arrangement as shown herewith. Notice that (if we omit the first one, H) the atomic weights of the next seven have a nearly regular increase, each varying from the preceding by not far from two. The next seven vary in much the same way, and so for the next series of seven elements. There is not a constant difference in the atomic weights, but the approximately regular increase is remarkable, especially when we see that the chemical properties of the elements can be told by knowing their atomic weights. But why are the elements arranged in series of seven? Na, the eighth, resembles Li, the first, in its properties much more than it does any other of the first seven elements; also Mg has properties quite similar to Cl, but different from the others of the series. Al is much like B, Si like C, P like N, S like O, Cl like F. These resemblances make the elements naturally fall into groups, the members of each group having similar properties. In the next series K falls into the same group as Na and Li; Ca as Mg, Cl, etc. Mendelejeff arranged the elements in a table, three series of which are shown below. This table should be carefully studied as regards groups, series, atomic weights, and properties of the elements. Note that in Group I the elements are very metallic, that in Group VII they are mostly non-metallic, and that in the intermediate groups there is a gradation from the strongly metallic to the strongly non-metallic. The valence of the members of each group should be noted. The elements of the first three groups show so little disposition to combine with hydrogen that their hydrides are almost unknown; but they do unite with chlorin, and their valence can be noted in their chlorides, while members of the last four groups combine with hydrogen.

	SYM.	WT.
	H	1
1	Li	7
2	Cl	9
3	B	11
4	C	12
5	N	14
6	O	16
7	F	19
8	Na	23
9	Mg	24
10	Al	27
11	Si	28
12	P	31
13	S	32
14	Cl	35
15	K	39
16	Ca	40
17	Sc	44
18	Ti	48
19	V	51
20	Cr	52
21	Mn	55

Explanation.—In the following table R stands for any metallic or plus element. The valence of the members of the different groups when they combine with oxygen is often different from that in the hydrogen and chlorin compounds. The oxids given are the highest possible to the group. F does not form an oxid. The student should write out the

symbols of the chlorids (or hydrids) of each element in the series below ; also the oxids of each.

PERIODIC TABLE (PARTIAL).

SERIES.	GROUP I.	GROUP II.	GROUP III.	GROUP IV.	GROUP V.	GROUP VI.	GROUP VII.
Hydrids or Chlorids.	RCl	RCl ₂	RCl ₃	RH ₄	RH ₃	RH ₂	RH
Oxids.	R ₂ O	R ₂ O ₂	R ₂ O ₃	R ₂ O ₄	R ₂ O ₅	R ₂ O ₆	R ₂ O ₇
1	Li	Gl	B	C	N	O	F
2	Na	Mg	Al	Si	P	S	Cl
3	K	Ca	Sc	Ti	V	Cr	Mn

280. Compounds. — Not only do the elements of any given group resemble each other, but their corresponding compounds have strong likeness; *e.g.*, LiCl is much like NaCl and KCl; also the three oxids of Group I are more nearly alike than they are like the oxids of any other group. The same thing is true of hydroxids and of other compounds belonging to the same group. The further the groups are separated the more dissimilar their elements and compounds seem to be. The hydrates of the members of Group I are distinctly basic in character; those of Group II are less so, and of III still less, while the oxyhydrogen compounds of Groups VII, VI, etc., are acidic, but proportionately less acidic as one goes from VII towards I. NaOH is a much stronger base than Al(OH)₃, and HClO₃ is a stronger acid than H₄SiO₄. The elements and compounds of the same group differ also in properties, according to the position in the group, whether near the top or the bottom, as the atomic weight increases. A still further division was made by Meyer,

who separated each group into two parts, *A* and *B* (Table, p. 199). The members of *A* in any group resemble each other more than they resemble the members of *B*; *e.g.*, Ca, Sr, Ba (Group II, *A*), are more nearly alike in chemical properties than they are like Zn, or Cd (Group II, *B*). Group I contains among others the alkali metals, Group II the alkaline earths. Group VII contains the halogens. The first few series contain elements having the smallest atomic weights, the last series those with largest atomic weights. The eighth series is entirely wanting, and the seventh and ninth contain the rare earths, several of which have never been isolated (see Appendix).

MEYER'S TABLE.

Series	A I	B A II	B A III	B A IV	B A V	B A VI	B A VII	B VIII
1	Li 7	Gl 9	B 11	C 12	N 14	O 16	F 19	
2	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35	
3	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56 Co 58 Ni 58
4	Cu 63	Zn 65	Ga 69	Ge 72	As 75	Se 78	Br 80	
5	Rb 85	Sr 87	Y 88	Zr 90	Cb 93	Mo 96		Ru 101 Rh 102 Pd 106
6	Ag 107	Cd 111	In 113	Sn 118	Sb 120	Te 126	I 126	
7	Cs 132	Ba 136	La 138	Ce 139				
8								
9		E 165.	Yb 172		Ta 181	W 183		
10	Au 196	Hg 199	Tl 203	Pb 206	Bi 207			Os 190 Ir 192 Pt 193
11				Th 231		U 238		

281. Prediction and Discovery.—If we regard the atomic weights of three members in three successive groups, *e.g.*, Li 7, Gl 9, B 11, the weight of the middle member may be found by taking the

mean of the other two $(7 + 11) \div 2 = 9$. This principle is only approximately true, as may be seen by trial with several elements, but it forms the basis for predicting unknown elements. Suppose Gl were not known. Its place in Group II would be vacant, but we should know that an element having an atomic weight of about 9 ought to be found, and that when found it would be metallic, and have properties much like those of Mg and Ca; its valence would be two, etc. The element Sc was discovered in 1879, but Mendelejeff had previously, 1871, announced that an element (which he named eka-boron) should be found with atomic weight 44, and properties between Al and Ga on the one hand and Ca and Ti on the other. A comparison of the properties of the element predicted with those of scandium afterwards found is given below.

Eka-boron, Eb; Predicted.

1. Atomic weight about 44.
2. Oxid, Eb_2O_3 , soluble in acids, analogous to Al_2O_3 but more basic, insoluble in alkalis.
3. Salts colorless, and give gelatinous precipitates with NaOH or Na_2CO_3 .
4. Sulfate, $Eb_2(SO_4)_3$, will form a double salt with K_2SO_4 , not isomorphous with alums.

Scandium, Sc, Discovered.

1. Atomic weight 44.
2. Oxid, Sc_2O_3 , soluble in strong acids, analogous to Al_2O_3 but much more basic, insoluble in alkalis.
3. Salts colorless, and give gelatinous precipitates with NaOH or Na_2CO_3 .
4. Sulfate, $Sc_2(SO_4)_3$, forms a double salt with K_2SO_4 , which is not isomorphous with the alums.

Several other elements have also been foretold by a similar application of the Periodic Law, and afterwards discovered. Many gaps are still left of elements as yet unknown, which it is quite likely may sometime be filled. The whole of series 8 is wanting. Most elements discovered of late exist in rare minerals, and are only chemical curiosities.

Table, p. 199, shows that following the third series, ending with Mn, there are other elements, Fe, Co, Ni, which are placed in Group VIII. Series 6 and 10 have also members placed in the same group. It will thus be seen that there are two short series of seven groups, followed by a long series of eight, then one short followed by a long series, etc. The entire list is best represented as a spiral. If this table were to be removed and folded into an octagonal prism, the appearance would be more nearly correct.

Though the Periodic Law is not as completely understood nor as perfect in its present statement as many other laws, *e.g.*, that of Definite

Weight, yet it serves the great purpose of enabling us to make a natural classification of elements; and changes chemistry from a mass of disjointed facts to a connected science; in several instances it has served to correct atomic weights and to verify some which were uncertain.

Exercises. — (1) In case an element should be found to fill the space in Group VII, Series 5, state what would be the symbol of its chlorid; its highest possible oxid; would the element be metallic or non-metallic? would it form a compound with hydrogen? State approximately its atomic weight.

(2) If an element should be discovered in Group IV, Series 9, state some of its leading properties, as in (1).

(3) Would an element in Group V, Series 11, be more or less metallic than Bi? State its approximate atomic weight, also its valence.

CHAPTER XXVI.

THE HALOGENS.

CHLORIN.

282. Chlorin is one of the very strongest of oxidizing agents; it has intense affinity for hydrogen and for most metals, with which it forms chlorids; it is a greenish yellow gas two and a half times heavier than air, and corrosive and poisonous in the extreme.

283. History.— It was first found in 1774 by Scheele, on mixing muriatic acid with manganese dioxid, but not till the nineteenth century was its true nature known. Scheele called it *dephlogistogated muriatic acid*, i.e., muriatic acid minus phlogiston. Berthollet named it *oxidized muriatic acid*, fancying it to be a compound, because he saw that its solution in water gave muriatic acid and oxygen when placed in sunlight. Gay Lussac and Thénard showed that one volume of it united with one volume of hydrogen to form hydrochloric acid. Davy, 1811, named it *chlorin* and ascertained its true character. Berthollet first proposed it as a bleacher of cloth.

284. Occurrence.— The affinities of chlorin are so strong that it never occurs free. Its most abundant compounds are chlorids, of which sodium chlorid, NaCl , and magnesium chlorid, MgCl_2 , are most common and widely distributed. The former is found in sea water, inland lakes, and beds or deposits from which it is dug like coal. The latter is a smaller constituent of sea water and of some mineral springs. Sea water contains nearly 3% of

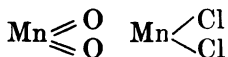
sodium chlorid, while some salt lakes are saturated with it, and from these it is gradually deposited, as the water evaporates. All soils and earth contain some sodium chlorid. Water percolating through these dissolves small portions of the salt, and—flowing into lakes with no outlet—evaporates, leaving a more and more concentrated and finally saturated solution.

Only one large deposit of potassium chlorid is known, *viz.*, at Stassfurt, Germany.

285. Preparation.—For laboratory or lecture-room experiments, chlorin is best made from hydrochloric acid, HCl, by introducing some substance which has an affinity for the hydrogen. Manganese dioxid, MnO_2 , is found to serve this purpose best, the hydrogen of the acid uniting with the oxygen of the oxid to form water.



Chlorin has affinity for metals, and so half of the Cl unites with manganese. We might expect that $\text{MnCl}_4 + 2\text{H}_2\text{O}$ would be the products, but one atom of Mn cannot hold more than 2 atoms of Cl, and half the Cl is thus set free, having nothing to combine with, while all the O goes to form water. It will be seen that the valence of Mn in the factors is four, in the products it is two, or that towards oxygen Mn has valence 4, towards chlorin 2. This is a reduction, and HCl is the reducing agent.



Exp. 158.—[*Caution.* Chlorin is so poisonous and irrespirable that it should always be prepared under a hood or where there is a draught of air, and very little must be allowed to get into the air of the room. Sprinkle a little NH_4OH on a warm plate to neutralize its effect. If any is

accidentally breathed, alcohol inhaled from a handkerchief is an antidote.]

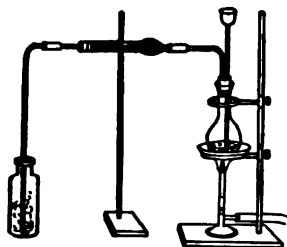


FIG. 107.

Arrange the apparatus as in Fig. 107. A drying tube of calcium chlorid is used, as for many experiments the dry gas is better. Put into the flask about 10 or 15^g of granular manganese dioxid, MnO_2 , and pour in 30 or 40^{cc} of HCl . Shake the mixture very thoroughly and apply gentle heat. Collect the gas by downward displacement, using large receivers. Keep watch, holding a piece of white paper behind the receivers, to see when the latter are nearly full. If a white gas finally evolves, add more

HCl , pouring out the first. The receivers should be kept covered with a glass plate. Pass some of the Cl into a solution of sodium hydrate, NaOH , in a test tube. This forms NaClO , sodium hypochlorite, and keeps the gas from the air. $2\text{NaOH} + 2\text{Cl} = \text{NaCl} + \text{NaClO} + \text{H}_2\text{O}$.

Exp. 159. — Pass some of the gas into water and into tubes in which there are solutions of litmus, carmine, indigo, etc.

Chlorin can be prepared in various other ways. (1) By heating a mixture of sodium chlorid, sulfuric acid, and manganese dioxid. The first two of these give rise to muriatic acid; and this, acting on the dioxid, gives chlorin. $2\text{NaCl} + \text{MnO}_2 + 2\text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} + 2\text{Cl}$. Note that the two metals combine with SO_4 , and the O with the H , leaving Cl free. (2) By acting on bleaching powder, CaCl_2O , with an acid. An apparatus like Fig. 108 is employed, the powder being put into the small beaker, the acid poured through the thistle tube, and the gas confined in the large beaker. (3) By heating $\text{K}_2\text{Cr}_2\text{O}_7$, potassium bichromate, and HCl . $\text{K}_2\text{Cr}_2\text{O}_7 + 14\text{HCl} = 2\text{KCl} + 2\text{CrCl}_3 + 7\text{H}_2\text{O}$

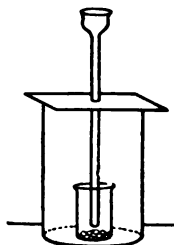


FIG. 108.

+ 6Cl . For analytical purposes *euchlorin*, a mixture of Cl and ClO_2 , is used, made by adding a few drops of HCl to crystals of KClO_3 , heating a moment, and then adding H_2O to dissolve the gases. $\text{KClO}_3 + 2\text{HCl} = \text{KCl} + \text{H}_2\text{O} + \text{ClO}_2 + \text{Cl}$.

286. On the Large Scale Cl is made by the Weldon process. The only difference of this process from the MnO_2 and HCl method first

described consists in transforming the MnCl_2 of the product into a compound that can be again treated with HCl . MnCl_2 was formerly wasted, hence the cost of Cl (made into bleaching powder, etc.) was considerable, as new MnO_2 had to be obtained each time. MnCl_2 is, by Weldon's process, treated with slaked lime. $\text{MnCl}_2 + \text{Ca(OH)}_2 = \text{Mn(OH)}_2 + \text{CaCl}_2$.

A mixture of lime and manganese hydrate with oxygen gives CaMnO_3 , calcium manganite ($\text{CaO} \cdot \text{MnO}_2$). $\text{Ca(OH)}_2 + \text{Mn(OH)}_2 + \widehat{\text{O}} = \text{CaMnO}_3 + 2\text{H}_2\text{O}$. This manganite is acted on by HCl . $\text{CaMnO}_3 + 6\text{HCl} = \text{CaCl}_2 + \text{MnCl}_2 + 3\text{H}_2\text{O} + 2\widehat{\text{Cl}}$. By this process the Mn , which is the costly ingredient, can be used again and again. The oxygen of air—together with steam—is forced into the mixture of hydrates and water.

287. Properties. — *Physical.* It is a gas, green-yellow in color, very stifling, corrosive, irrespirable, and poisonous. If it were breathed in quantity, death would result. Its density is about 35. It is quite soluble in water, to which it imparts a yellow color.

Chemical. One of the most active of elements, having great affinity for hydrogen and for metals, as well as many non-metals, it attacks almost everything. Mixed with hydrogen and brought into sunlight, it combines with explosive violence, but does not combine in darkness. In diffused light it slowly unites. Hydrogen burns in the gas. Hydrochloric acid, HCl , is the product in each of the above cases. Many metals, like Sb , Cu , As , etc., burn in it and give rise to their chlorids. $\text{Sb} + 3\widehat{\text{Cl}} = \text{SbCl}_3$. $\text{Cu} + 2\widehat{\text{Cl}} = \text{CuCl}_2$. It attacks gold, brass, etc. *Dutch metal*, an alloy of Cu and Zn , burns in chlorin. The hydrogen of turpentine, C_6H_6 , has such affinity for it as to burn with a flash when in contact with it, and throw off volumes of black carbon. $\text{C}_6\text{H}_6 + 6\widehat{\text{Cl}} = 6\text{HCl} + 6\text{C}$. Cl in solution in water will gradually combine with the H and liberate O , which may be collected at the top of

a tube, the HCl formed being dissolved in the H_2O . Sodium, mercury, phosphorus, etc., heated in an open

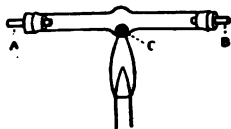


FIG. 109.

bulb tube, with a jet of chlorin passing over them (Fig. 109) combine with the yellow gas to form chlorids. Chlorin bleaches most vegetable and animal pigments, litmus, indigo, calico prints, etc., and the bleaching is per-

manent. Dry fabrics are bleached scarcely at all, from which it is supposed that the Cl unites with hydrogen of the water, and liberates the oxygen, which in the nascent (or the ozone) state attacks the coloring matter and breaks up its molecule. Carbon colors, like printer's ink, and mineral pigments, *e.g.*, PbCrO_4 , chrome yellow, it does not bleach. Chlorin at a white heat breaks up into its atoms, its vapor density being then half its atomic weight, and its molecule being Cl , while at ordinary temperatures it is Cl_2 .

288. Bleaching.—Cotton cloth is bleached by passing long rolls of it through successive vats, the first, third, fifth, etc., of which contain water acidulated with H_2SO_4 , the second, fourth, etc., contain a solution of bleaching powder, CaCl_2O . A very little acid is left on the cloth as it passes through the first vat. This acid liberates Cl from the CaCl_2O in the second, and the Cl partially whitens the cloth. In the successive vats the same operation is repeated till the fabric is of the requisite color.

Exp. 160.—Put some powdered antimony into a small cloth bag, and shake the bag over a receiver of dry chlorin. Stibnite, Sb_2S_3 , will also burn.

Exp. 161.—Fasten a leaf of *Dutch metal* rolled loosely to one end of a wire and lower it into a receiver of dry chlorin.

Exp. 162.—Put a piece of sodium into a combustion cup, set it on fire, and lower it quickly into a receiver of chlorin. Try the same with phosphorus.

Exp. 163. — Dip a piece of paper into spirits of turpentine, *slightly* warmed in an evaporating dish, and with forceps thrust it into a receiver of chlorin.

Exp. 164. — Prepare a philosopher's lamp with tubes as in Fig. 110. After testing and lighting the hydrogen gas, lower the flame into a receiver of chlorin.

Exp. 165. — Put some dry figured calico, turkey red cloth, etc., into a receiver of dry chlorin. If these do not bleach after some time, add a little water and shake them up with it and the gas.

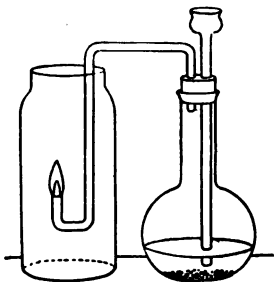
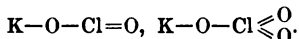


FIG. 110.

Exp. 166. — *Euchlorin*. Add to 3 or 4 crystals of potassium chlorate, KClO_3 , a few drops of HCl , hold the tube containing them in the flame for a moment, and when the tube fills with gas add water. Test the bleaching properties of this on the substances in the previous experiment.

Exp. 167. — Add a single drop of euchlorin to a mixture of starch and KI solution. Also to a mixture of starch and KBr solution.

289. Compounds. — In binary compounds, *i.e.*, chlorids, the valence of chlorin is one, as KCl , HCl , CaCl_2 , SbCl_3 , CCl_4 . In ternaries it often has other valences, as five in KClO_3 , three in KClO_2 , etc.



Potassium hypochlorite, KClO , and potassium chlorate, KClO_3 , are both made by passing chlorin into KOH solution. The first case requires cold dilute hydrate solution, the second concentrated. (1) $2\text{KOH} + 2\widetilde{\text{Cl}} = \text{KCl} + \text{KClO} + \text{H}_2\text{O}$. (2) $6\text{KOH} + 6\widetilde{\text{Cl}} = 5\text{KCl} + \text{KClO}_3 + 3\text{H}_2\text{O}$. Bleaching powder is made by passing Cl into slaked lime. $2\text{Ca}(\text{OH})_2 + 4\widetilde{\text{Cl}} = \text{Ca}(\text{ClO})_2 + \text{CaCl}_2 + 2\text{H}_2\text{O}$. Bleaching powder is either a mixture of $\text{Ca}(\text{ClO})_2 + \text{CaCl}_2$ or CaCl_2O , which of the two is uncertain. $\text{Ca}(\text{ClO})_2 + \text{CaCl}_2 = 2\text{CaCl}_2\text{O}$. Tests for chlorids were given in the treatment of HCl .

290. Uses. — The main applications of chlorin are in making bleaching powder, chlorates, chlorids, chloroform, CHCl_3 , and as an oxidizing agent in the laboratory.

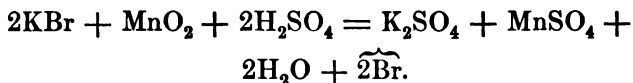
BROMIN.

291. This is the only liquid non-metallic element. Of a deep-red color and very volatile, it is three times heavier than water, and its vapor weighs five times more than air, and 80 times more than hydrogen. Its name, from the Greek, means a stifling odor. The element is very much like Cl in most of its properties.

292. History. — Balard, 1826, first isolated bromin, obtaining it from the mother liquor of sea water. It was the last non-metal discovered previously to fluorin, 1886, and argon, 1894.

293. Occurrence. — Restricted and not abundant in its compounds, bromin never occurs uncombined. America and Germany have the largest supply. In the former country the salt wells of West Virginia and Ohio supply the bulk of bromin and its compounds, while the potassium chlorid mines of Stassfurt yield considerable. It exists in small amounts in sea water. The compounds in which it exists are sodium, potassium, and magnesium bromids, NaBr, KBr, MgBr₂.

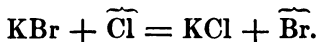
294. Preparation. — In the laboratory it is liberated from its most common compound, potassium bromid, KBr, by the action of manganese dioxid, MnO₂, and sulfuric acid, H₂SO₄, precisely like Cl from NaCl.



Notice that oxygen and all the hydrogen combine to form water, and that each metal forms a sulfate, leaving Br free (compare Cl and I).

295. On the Large Scale from Brine Springs.—

The water is partially evaporated leaving NaCl to crystallize out. The thick liquid left (called *bittern* or *mother liquor*) and containing in solution salts like MgBr_2 , is separated from the crystals, and to it are added MnO_2 and H_2SO_4 . Heating gives the same reaction as above, in addition to which some Cl is set free from the NaCl. This reacts with MgBr_2 , NaBr, KBr, and liberates Br.



Exp. 168. — [Care must be taken not to get Br gas into the air of the room. Experiments should be made at the hood. Use the same antidote as for Cl.] Mix two or three grams of potassium bromid with an equal amount of manganese dioxid, and add to them in a test tube a very little sulfuric acid diluted with two-thirds its volume of water. Attach

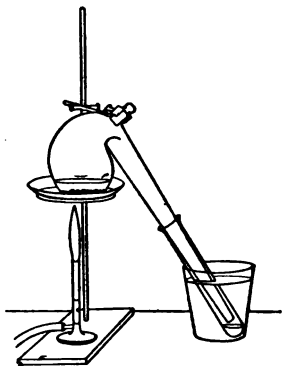


FIG. 111.

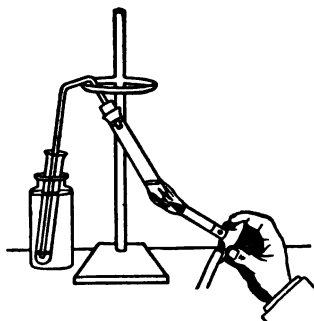


FIG. 112.

a cork and delivery tube, heat the contents, and collect the liquid in a test tube surrounded by water (Fig. 112), or use a retort (Fig. 111). Disconnect the stopper, and pour a little of the gaseous Br into a tube containing a little starch solution.¹ Note the weight of the gas, and, after shaking the tube, the color of the starch. Save the bromin.

¹ Starch solution, or paste, is made by moistening a very little powdered starch, pouring on considerable boiling water, and reboiling the mixture. For these tests it should be thin.

Exp. 169.—To a solution of potassium bromid add a few drops of euchlorin, and shake them. The free Br in the KBr and Cl solution can be observed by shaking up a little ether with it. The ether rises and carries up the Br.

296. Properties.—*Physical.* At usual temperatures it is a thin, volatile, deep-red liquid which freezes at -7° , but evaporates rapidly at all temperatures above that. Its specific gravity is about 3, and vapor density 80. It is a very poisonous, irritating, irrespirable gas, which attacks all the membranes, and especially the eyes. The liquid burns into the flesh and makes sores very difficult to heal. It is somewhat soluble in water (the solution being known as *bromin water*), but more so in alcohol, ether, or carbon disulfid.

Chemical. It has great affinity for hydrogen and for metals, with which it forms bromids, as HBr, AgBr, SbBr₃, etc. Its solution in water, like Cl, gradually combines with the hydrogen, setting free oxygen when exposed to sunlight, but a mixture of H and Br gases has to be heated before the two will combine. Chlorin will also break up bromids from solution, liberating Br and combining with the other element. $\text{KBr} + \widehat{\text{Cl}} = \text{KCl} + \text{Br}$. It will successively replace the atoms of H in such compounds as C₆H₆, forming C₆H₅Br, C₆H₄Br₂, etc., as Cl does. A piece of antimony thrown into Bromin burns vigorously, forming SbBr₃. It will not combine with oxygen, and no oxid of Br is known. With KOH it forms KBr and either KBrO or KBrO₃ as with Cl. Its main salt, from which others are made, is KBr, potassium bromid. Silver bromid, AgBr, is another important one, made by mixing solutions of KBr and AgNO₃. $\text{KBr} + \text{AgNO}_3$

$= \text{AgBr} + \text{KNO}_3$. At about 1200° the bromin molecule is dissociated into its atoms.

Exp. 170. — Add a drop or two of Br to 2 or 3^{cc} of H_2O . Is it soluble?

Exp. 171. — Add a drop or more of bromin water to a solution of litmus, indigo, or carmine.

Exp. 172. — Add a few drops to a little silver nitrate solution, AgNO_3 . Divide the product into two parts. To (1) add HNO_3 , to (2) add NH_4OH . (1) is insoluble, (2) is slightly soluble.

Exp. 173. — Into a tube containing 5^{cc} H_2O pour a few drops of KBr solution. Add one or two drops of carbon disulfid, CS_2 . Now add one drop of euchlorin and shake the mixture. Euchlorin frees Br, which the CS_2 dissolves, carrying it to the bottom, where it is seen as a brown-red globule.

Exp. 174. — Put a drop of KBr solution into 5^{cc} H_2O , with a little starch solution, add a drop of euchlorin, and shake the whole. The Br set free by Cl should color the starch yellow or orange. The above experiments serve as tests for Br and bromids.

297. Uses. — Bromin is used somewhat in manufacturing anilin colors and in organic chemical analysis. Potassium bromid finds employment in medicine and is the basis of other bromin compounds. Silver bromid the photographer uses especially for the *negative*. Magnesium bromid is found in some mineral waters.

IODIN.

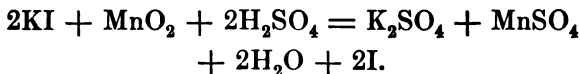
298. Seaweeds were formerly burned and their ashes, called *kelp*, were used in making glass, soap, etc., on account of the sodium carbonate they contained. An observant French soapmaker named Courtois discovered in the ashes a new substance, which he submitted to a chemist for examination. It proved to be an element

which, vaporized, was of a beautiful violet color, and on that account was named, from the Greek, *iodin*. A ton of ashes may yield ten pounds of iodine, and as much more may be wasted. Only two species of marine plants contain enough for profitable extraction.

299. History. — Courtois discovered it in 1811. Davy and Gay Lussac in 1815 showed it to be an element.

300. Occurrence. — Iodine does not occur free. Its compounds are widely distributed, but are not abundant. A very minute quantity is distributed in sea water, from which certain marine plants take it up. Until a short time ago the main source of the iodine of commerce was seaweed, but now the nitrate deposits of Chile furnish far the largest proportion. Sodium iodate, NaIO_3 , and iodide, NaI , are compounds occurring with sodium nitrate, NaNO_3 .

301. Preparation. — For laboratory work and for separation on a large scale, the same method is employed as for the similar elements Cl and Br, *viz.*, heating the iodide with MnO_2 and H_2SO_4 .



Chlorine is also sometimes used, as described under *bromine*, for the same purpose. The affinity of hydrogen for iodine is so weak that sulfuric acid alone with potassium iodide liberates iodine for the most part, instead of forming HI .

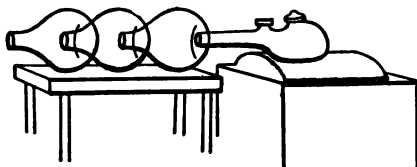


FIG. 113.

Fig. 113 shows the sublimation of iodine on a large scale in vessels called aludels.

Exp. 175. — Put into a test tube about a gram of potassium iodid, KI, and as much manganese dioxid, MnO_2 . Cover it with H_2SO_4 and warm the mixture. Hold an open tube inverted over the tube containing the mixture. Observe the color of the vapor and the sublimate.

Exp. 176. — Pour a few drops of euchlorin into a solution of KI. Add Br to KI solution.

302. Properties. — *Physical.* Iodin is a heavy, grayish-black solid of metallic lustre, crystallizing in rhombic scales, being seldom amorphous or liquid. A crystal in the hand stains it brown and slowly vaporizes. Its vapor is of a violet to purple color, 126 times heavier than hydrogen, but at higher temperatures only 63 times, showing its molecule to have sometimes one atom, sometimes two.

Water dissolves it but slightly, alcohol and carbon disulfid readily. It also dissolves in a solution of potassium iodid, KI. Tincture of iodine consists of the element dissolved in alcohol, $\text{C}_2\text{H}_5\text{OH}$.

Chemical. The properties of chlorin, bromin, and iodine are quite similar, the affinities of bromine are less strongly marked than those of chlorin, of iodine less than the other two. Iodine has some affinity for hydrogen and the metals, making with the former, hydriodic acid, HI, with the latter, iodids, as PbI_2 . It also is combined with oxygen to form I_2O_5 , the pentoxid, or anhydrid of iodic acid, HIO_3 . $\text{I}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{HIO}_3$. It combines vigorously with phosphorus, forming PI_3 . A compound of N and I, NI_3 , explodes at the touch of a feather. Iodine colors starch solution blue, an iodid of starch being the supposed product. Heat breaks up the compound and destroys the color, which is restored on cooling. Compounds of iodine will not give this result. It is therefore a very delicate

test for iodine. Iodides must first be broken up by chlorine, ozone, etc., when the free iodine responds to the test. Iodine molecules begin to dissociate into their atoms at 600° .

Exp. 177. — Hold a crystal of iodine in the fingers for a moment and notice the stain. Drop it into a dry test tube and bring the tube to a flame. Observe the vapor, and pour a little into another tube containing a thin solution of starch. Shake the latter and observe the color. Note also any crystals of sublimed iodine in the first tube.

Exp. 178. — Try the solubility of one or two iodine crystals in 5 cc of hot water. Pour a drop of this into a thin solution of starch. Pour off the water, leaving the crystals, then add 2 or 3 cc of alcohol, C_2H_5O . Does the iodine dissolve? Apply the starch test. Test the solubility of I in potassium iodide solution.

Exp. 179. — Cover a crystal or two of iodine with carbon disulfide, CS_2 , in an evaporating dish, and notice the solution. Place in a draft of air, and observe the evaporation and formation of crystals.

Exp. 180. — To lead nitrate solution, $Pb(NO_3)_2$, add KI solution. Boil it, and watch the result on cooling.

Exp. 181. — Heat in a tube one or two crystals of iodine with the same amount of mercury. Observe any combination or sublimate.

Exp. 182. — Place on a piece of wood a little iodine and upon this a dry piece of phosphorus.

Exp. 183. — Place a bit of pulverized iodine in an evaporating dish, cover it with NH_4OH and leave for half an hour. Filter it, then open the filter paper, and when it is dry, a slight agitation will produce an explosion, caused by breaking up of NI_3 into its elements.

303. Uses. — The world uses between half a million and a million pounds of iodine yearly. A part of it goes as medicine, (tincture and potassium iodide), some is used in manufacturing aniline colors, and the chemist consumes some in his laboratory. But little is now used in photography as silver iodide, whereas much was formerly employed.

Tests for Iodides. — These are two, the *starch* test and the *carbon disulfide* test; they consist in liberating the iodine and testing that.

Exp. 184. — A few drops of KI solution are put into 5 or 10^{cc} of H₂O, a very little starch solution is added, then it is shaken, and one drop of euchlorin is put in. A blue color shows the test.

Exp. 185. — To a little KI solution in water add two drops of carbon disulfid, CS₂, then one or two drops of euchlorin. Shake the mixture. The Cl liberates iodine, which the CS₂ dissolves and which imparts a violet color to the CS₂ in the bottom of the tube; this is decolorized by NaOH.

✓**304. Fluorin.** — Fluorin is chemically the most violently active of all known elements. It combines with all of the common elements except oxygen, platinum, and gold. Its compounds, fluorite, CaF₂, and cryolite, Na₃AlF₆ (both of which occur native), as well as the acid HF, have been known for a long time, but the element was not known until Moissan in 1886 isolated it, for as soon as set free from one compound it would form another. It can be separated from its compounds by electrolysis, from liquid hydrofluoric acid (which contains potassium fluorid) in a platinum dish. It is a light yellowish gas of strong, irritating odor, has great affinity for hydrogen, and quickly decomposes water or silica. The enamel of the teeth contains a compound of fluorin. The only important use of the element is in the compound HF, the agent for etching glass.

305. The Halogens Compared. — The elements fluorin, chlorine, bromine, iodine, form a natural group, as shown by the Periodic System. The variation and comparison of their properties should be noted.

1. Similarity of origin. Salt water is the ultimate source of all except fluorin; Cl comes from sea salt, Br from brine springs, I from seaweed.

2. Similarity of valence. In binary compounds each is a monad.

3. Likeness of preparation. All except F are obtained from their salts by means of MnO₂ and H₂SO₄.

4. Variation in color, state, and vapor density. F is a light yellowish gas, Cl a heavy greenish yellow gas, bromine a volatile, red liquid, I a dark, crystalline solid. The vapor densities are F 19, Cl 35, Br 80, I 126.

5. Variation in chemical activity in inverse ratio to the vapor density. F is most active, Cl next, then Br, and lastly I. Their hydrogen acids HF, HCl, HBr, HI exhibit a corresponding gradation in strength or activity. Fig. 114 illustrates this decreasing affinity, A representing that of fluorine, B of chlorine, C of bromine, and D of iodine.

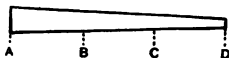


FIG. 114.

CHAPTER XXVII.

VAPOR DENSITY, MOLECULAR WEIGHT, ATOMIC WEIGHT.

306. As a first step in obtaining the *atomic weight* of a gaseous element, as well as the *molecular weight* of either element or compound, it is necessary to know the weight of a unit volume of it as a gas, and to compare that weight with some standard. The standard or unit of comparison is hydrogen, that being the lightest, volume for volume, of known gases. Such a comparison of weights gives us *vapor density* (called simply *density* when applied to permanent gases). In this chapter we shall explain how, from the analysis of a compound, we may obtain its symbol. This involves a knowledge of the relations between vapor density, molecular weight, and atomic weight. Chap. XIX should be reviewed at this point.

307. History. — Dumas, about 1827, was the first to devise an accurate method of obtaining vapor densities. Dalton worked upon a series of atomic weights, first published in 1805 by Thompson, and in 1808 by the author himself, but they were very crude. Berzelius, 1826, made a corrected list. Since that time Dumas, Stas, and F. W. Clarke may be mentioned as prominent in bringing atomic weights to their present state of perfection. Dumas, Gay Lussac, and Victor Meyer have devised distinct methods of obtaining densities.

308. Density. — *The density of any gas is the weight of a certain volume of it in terms of the weight of an equal volume of hydrogen, at the same temperature and pressure.*

It has been found convenient to reduce all volumes to what they would be at 0° and 760^{mm} pressure. This is called normal temperature and pressure, N.T.P. A liter of hydrogen, N.T.P., weighs .0896^g, a liter of oxygen 1.43^g, one of iodine vapor 11.29^g, of steam .8064^g. The weight of a liter of hydrogen, .0896^g, is called a crith. A liter of oxygen weighs 16 criths. Now the ratio of the weight of hydrogen to that of oxygen is .0896 : 1.43 :: 1 : 16 $\left(\frac{1.43}{.0896} = 16 \right)$, hence the vapor density (v.d.) of oxygen is 16 ; of steam (.0896 : .8064 :: 1 : 9) is 9. These weighings must be made at the same temperature and pressure, or the results reduced to the same. As water or iodine would not be gases at 0° , weighing is done at a higher temperature. The result may be reduced to N.T.P. Meyer has found vapor densities at as high as 1700° . Many substances are either not vaporized under conditions which make weighing possible (*e.g.*, carbon), or are dissociated (*e.g.*, ammonium chlorid), and in other cases it is difficult to obtain exact results, at high temperatures. Hence the molecular weights — which depend upon vapor densities — of many elements and compounds are uncertain, and the molecular symbols are the simplest which represent percentage composition. There are, however, other methods of approximating to these symbols besides the vapor density method.

Many elements which have a certain density taken at one temperature and reduced to N.T.P. have a very different one when reduced from another temperature. Sulfur vapor at 1000° has v.d. 32, while at 500° it has 96. This, we shall see, varies the molecular weight.

Some other elements which vary are given under Atomic Weights.

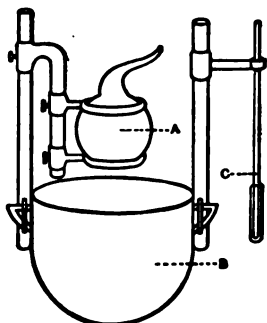


FIG. 115.

309. Dumas' Method. — The two best methods to obtain vapor density are one devised by the French chemist Dumas, and one by the German Victor Meyer. The apparatus for Dumas' method is shown in Fig. 115. It consists of a glass globe or matrass, *A*, the opening of which is drawn out to a fine point. Suppose we wish to obtain the density of alcohol vapor. A small quantity of liquid alcohol is introduced into *A*, which has been previously weighed, and which is now placed on a sliding frame, so as to be lowered into the vessel *B*, which holds a hot liquid — water, oil, paraffin, etc. A movable thermometer,

C, shows the temperature of this latter liquid, and a barometer in the room marks the pressure. *B* is heated, *A* is immersed (Fig. 116) to its neck in the hot liquid contained in *B*, which vaporizes the alcohol and drives out the air. The escaping alcohol is ignited, and when it is all vaporized, and the tension inside *A* equals that of the air, the light goes out. The tube is then sealed by means of a blowpipe, the readings of barometer and thermometer are taken, and *A* is removed, cleaned and dried, and afterwards weighed, pressure and temperature of air in room being again taken. The following data — certain details and reductions being omitted — show the principle. The globe holds exactly a liter, 1000^{cc}.

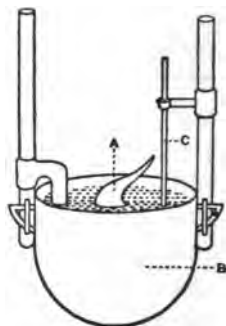


FIG. 116.

Weight of globe and air, N.T.P.	41.216 ^g
“ “ air, 1000 ^{cc} , N.T.P.	1.292 ^g
“ “ globe and vapor (sealed at 273°)	40.9544 ^g
“ “ 1 liter hydrogen (at 273°)	.0448 ^g

The weight of 1000^{cc} of air is known to be 1.292^g at N.T.P. Subtracting the weight of air from the weight of the globe and air, we obtain the weight of the globe (*in vacuo*). 41.216 — 1.292 = 39.924. Deducting

the weight of the globe from the weight of the globe and vapor gives the weight of the alcohol vapor. $40.9544 - 39.924 = 1.0304$. This was measured at 273° . A liter of hydrogen at 273° weighs half as much as a liter at 0° , or .0448g. Hence the v.d. of alcohol is 23, i.e., $1.0304 \div .0448 = 23$.

310. Meyer's Method. — This consists in weighing a small quantity of the liquid substance, then vaporizing it and noting the volume of air which the vapor displaces. The apparatus is seen in Fig. 117. *A* is an outer tube which ends in a bulb, *B*, and which contains a substance like anilin that vaporizes at a higher temperature than the liquid whose vapor density is required. The vapor in the outer tube keeps the temperature of that in the inner tube constant. *C* is the inner tube, the upper part of which is quite small, ending in a stoppered opening. This holds the liquid to be experimented upon. *E* is a side tube opening into a trough of water, in which there is also an inverted graduated tube, *F*, to hold the expelled air. Suppose alcohol to be the substance whose vapor density is wanted. The substance in the outer tube *A* is first vaporized and the excess of heated air in the inner tube *C* is driven out through *E* and discarded. As soon as the temperature becomes uniform and the surplus air is all expelled, a weighed quantity of liquid alcohol, say $\frac{1}{10}$ of a gram in a vial, is dropped into the tube *C* and the cork quickly replaced. *F*, which is filled with water, is moved over the opening of *E*, and as the alcohol rapidly vaporizes at the high temperature, it drives the air into the graduated tube *F*, where its volume is noted. This for $\frac{1}{10}$ of a gram — when reduced to N.T.P. — is 48.53cc. $\frac{1}{10}$ of a gram of hydrogen at N.T.P. occupies 1116cc. Hence the density of alcohol vapor will be in inverse ratio to these volumes, i.e., $1116 : 48.53 :: 23 : 1$.

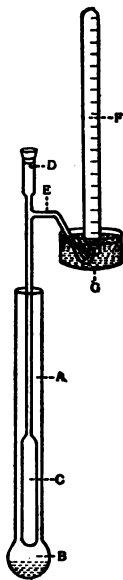


FIG. 117.

Exercises. — (1) A certain volume of hydrogen weighs .36g N.T.P. How many liters does it contain? If one liter weighs .09g, to weigh .36g will take $.36g \div .09g = 4$. Hence 4 liters.

(2) How many liters of hydrogen in 63g? In 2.7g? In 1g? 5g?

(3) If the gas were twice the vapor density of hydrogen, how many cubic centimeters in each of the above?

¹ The liter of hydrogen is taken as .09g in these and other problems.

- (4) How many liters of chlorine in each of the above numbers of grams?
- (5) How many of hydrogen chloride, HCl? Of CO?
- (6) A liter of chlorine weighs 3.195g. Compute its vapor density. V.d. being ratio of weights of equal volumes, we have $3.195 : .09 :: 35.5 : 1$.
- (7) Three liters of mercury vapor weigh 26.9g. Find the v.d. of Hg.
- (8) Five liters of CO_2 weigh 9.9g. Find the v.d. of CO_2 . Verify the result from the molecular weight.

For solving certain problems in which gases are involved, two additional laws may be stated. The first one is due to Boyle, 1660, and Mariotte, 1676, the second to Gay Lussac, 1808. The student is referred to some work on physics for further discussion of them than is here given.

311. Mariotte's Law. — *The volume of a given weight of any gas at a constant temperature varies inversely as the pressure to which it is exposed.*

A body of gas which occupies a liter under pressure of one atmosphere is reduced to half a liter under two atmospheres, or is expanded to two liters under pressure of half an atmosphere.

312. Absolute Temperature. — If a liter of a gas at 0°C. is raised 1° , its volume increases $\frac{1}{273}$; if 2° , $\frac{2}{273}$; if 273° , it doubles in volume. Lowering the temperature produces a like contraction; e.g., -1° reduces it $\frac{1}{273}$; -2° , $\frac{2}{273}$, etc. If this ratio continued to -273° , evidently the gas would occupy no volume at all, but be annihilated. Before reaching that point, however, all gases change their state and the law is no longer operative. This low point, -273°C. , is called the *absolute zero*, 0°A. , and temperatures reckoned from it are *absolute temperatures*. $0^\circ \text{C.} = 273^\circ \text{A.}$, and $0^\circ \text{A.} = -273^\circ \text{C.}$ Hence to change from C. to A. we add (algebraically) 273° .

313. Gay Lussac's Law. — *The volume of a given weight of any gas, under constant pressure, varies directly as the absolute temperature.*

A body of any gas which at 273° A. occupies a liter, at 546° A. would occupy 2 liters, the pressure being constant.

Exercises. — (1) What will be the volume of oxygen at 0° C. and 760^{mm} pressure which is 1450^{cc} at 27° C. and 758^{mm}? What its weight?

Solution. By application of the above laws the following compound proportion is formed. $27^{\circ} + 273^{\circ} = 300^{\circ}$. $\frac{300 : 273}{760 : 758} \left. \vphantom{\frac{300 : 273}{760 : 758}} \right\} :: 1450 : x = 1316^{\text{cc}}$.
 $1316^{\text{cc}} = 1.316^{\text{l}}$. $1.316 \times 16 \times .09 = 1.89\text{g}$.

(2) A gas occupies 2000^{cc} when the barometer stands 750^{mm}. What volume will it fill at 760^{mm}? (3) At 750^{mm} I have $4\frac{1}{2}^{\text{l}}$ of oxygen. How many liters at 730^{mm}? (4) At 825^{mm}? (5) At 200^{mm}? (6) Compute the volume of a gas at 70° which at 30° is 150^{cc}. (7) 3000^{cc} of oxygen at 0° will occupy what volume at 100° ? (8) I fill a flask holding 2^{l} with hydrogen, when the thermometer indicates 26° and the barometer 762^{mm}. What is the volume at 0° and 760^{mm}? (9) What should a liter of hydrogen at 273° weigh? (10) A liter of oxygen? (11) One of CO_2 ? (12) What would be the weight of 2^{l} of CO at 0° and pressure of half an atmosphere, i.e., 380^{mm}? (13) At 2 atmospheres?

314. Molecular Weight. — *The molecular weight of a gaseous substance is twice its vapor density. The vapor density is half the molecular weight.* If a liter of oxygen weighs 16 (or x) times a liter of hydrogen, it is evident that an atomic volume of oxygen weighs 16 (or x) times an atomic volume of hydrogen, since we thus compare the weights of equal volumes of two gases. It was shown (Chap. XIX) that a molecular volume \square is twice a hydrogen atom volume \square . Hence a molecular volume of any gas weighs twice an atomic volume of the same gas, or molecular weight is twice vapor density. The molecular

CO_2
 weight of CO_2 is 44, $\underbrace{12 + 32}_{44}$, the weight of one molecule \square . The vapor density is 22, the weight of \square .

Exercises. — The v.d. of bromin is 80, the molecular weight is 160. Find the molecular weight of each of the gases following, from the given vapor density: S = 32, As = 150, Zn = 32.5, N_2O_3 = 38, $C_{10}H_{16}$ = 68. See whether your result coincides with that obtained by using the atomic weights. Find the v.d. of these, first computing the molecular weights by affixing atomic weights: CO, NH_3 , C_2H_2 , HCl. The vapor density of acetic acid is found to be 29.7. See which, if any, of these symbols it corresponds to, the percentage composition being the same in all three: H_2CO , $H_4C_2O_2$, $H_6C_3O_3$. Find which of these symbols the v.d. 33.5 corresponds to: ClO_2 , Cl_2O_4 .

315. Atomic Weight. — It has been shown that molecular weight is obtained from vapor density. Atomic weight is not derived from either, but is obtained in a very different way. *The atomic weight of an element is its least combining weight, the weight of the smallest particle of it which exists in any compound or takes part in any reaction.* It is evident that we cannot ascertain the atomic weight of any element from a single compound, but must analyze as many compounds as possible, and ascertain the ones in which the smallest amount enters. This smallest weight will be the atomic weight, and all of the other compounds will contain a multiple of that weight.

Procedure. — Suppose we wish to find the atomic weight of oxygen from the compounds in the first column following.

	V. d.	Mol. wt.	Wt. of O.	Weight of other elem.	Sym.
Oxid of carbon	14	28	16	12	CO.
“ “ “	22	44	32	12	CO ₂ .
“ “ hydrogen	9	18	16	2	H ₂ O.
“ “ nitrogen	22	44	16	28	N ₂ O.
“ “ “	38	76	48	28	N ₂ O ₃ .
“ “ “	23	46	32	28	NO ₂ .

The first step in the process is to obtain the density, as above described, of each of the gases. The second is to obtain the molecular weight by doubling the density. In the third step the composition of

each gas must be determined by analysis. Different methods of analysis are made use of, dependent upon the affinities of the compound in question. This and the first step require the most refined manipulation and careful weighing with delicate balances. The last step consists only in noting the smallest proportion of oxygen by weight which enters into any of the compounds. This is seen — column 4 — to be 16, hence this is the atomic weight of the element. If in future any compound should be found in which the proportion of oxygen is 8, 4, or anything less than 16, that would be its atomic weight, for it would be its least combining weight. But to the present time none has been found. We here see one of the main reasons for supposing that atoms exist at all, for since there is a smallest combining weight for every element, and every known compound of that element contains it either in that proportion or some multiple of it, it is fair to suppose that there is a smallest indivisible particle, and to that supposed particle we give the name *atom*. The last column, symbols of the gases, is obtained by dividing the weight of each element in a molecule by its atomic weight, which gives the number of atoms of the elements in the given molecule.

316. Exact Weights. — Atomic weights have been used as though they were whole numbers, multiples of the unit hydrogen. This is the fact in only a very few cases. Results of experiments are probably not accurate beyond the second decimal place. Instead of making hydrogen the unit ($H = 1$) and referring all atomic weights to it, many chemists prefer to use oxygen as the standard ($O = 16$). The most refined experiments by the ablest chemists have been made to show this relation of hydrogen to oxygen. Many results have been obtained at different times. At first, with $H = 1$, oxygen was supposed to have an atomic weight of 16, then 15.96, etc., until at present it stands 15.879, on Morley's exhaustive determinations covering a period of twelve years.

317. Molecular and Atomic Volumes. — While the vapor density and the atomic weight of elements are obtained by different processes, yet the two results are generally identical, that is, with the few whose vapor density is known. But this is not always true, and it leads to interesting conclusions in regard to volumes of atoms. All molecular volumes, elementary and compound, are equal. Not so all volumes of atoms of elements. Oxygen has vapor

density 16 and hence molecular weight 32. Its atomic weight is 16, and there are therefore two atoms to the molecule (*i.e.*, molecular weight \div atomic weight). As the molecule is constant in volume \square , the oxygen atom volume \square is half the molecular volume. In the case of mercury the vapor density is $99\frac{1}{2}$, the molecular weight 199, and the atomic weight 199. Hence there is one atom to the molecule, and atom and molecule are identical \square . Arsenic, at usual temperatures, gives vapor density 150. The molecular weight must be 300, but atomic weight is 75, and this gives four atoms per molecule, which makes the arsenic atom volume one-fourth the molecular volume \square , or half the hydrogen atom volume.

318. Results. — O, N, H, F, have two atoms per molecule at all temperatures, Cl, Br, I, have two at ordinary temperatures, whereas at higher they each have only one. S at a high temperature has two, at lower, 6 or 8. P and As have four at a low temperature, at higher only two. Hg, Cd, Zn have one atom per molecule. Ozone has three. Sb has two or three, Bi one or two. The results on Na and K are not certain. Compounds of only about 45 elements have been weighed in the gaseous state. Hundreds of compounds of the four elements O, N, H, C have had their vapor densities taken, while not over half a dozen compounds of As, Hg, Sn, or Zn have been weighed as gases, and of the rest of the 45 not more than one each.

319. Symbols of Compounds. — To obtain the symbol (or formula) of a compound we should know (1) its percentage composition (*i.e.*, the per cent of each element in its composition); (2) the atomic weight of each of its elements; (3) its vapor density. From (1) and (2) alone we can obtain a symbol, some simple multiple of which is correct, but what multiple that is, the vapor density alone can determine. The accompanying examples illustrate the method.

Exercises. — (1) A liter of a compound gas weighs 1.26g. $\frac{1}{4}$ of it is carbon, $\frac{3}{4}$ oxygen. What is its formula?

Solution. Its v.d. is first found: $1.26 \div .09 = 14$. Next its molecular weight: $14 \times 2 = 28$. Then the amount of carbon and of oxygen per molecule: $28 \times \frac{1}{4} = 12$ (carbon). $28 \times \frac{3}{4} = 16$ (oxygen). The atomic weight of carbon is 12 and of oxygen 16, hence there is one atom of each in the molecule and the symbol is CO.

(2) A liter of a compound gas weighs 2.88g. Analysis shows that its weight is half sulfur and half oxygen. What is the symbol. (Atomic weights are to be taken from p. 16.)

(3) Two liters of a compound of N and O weigh 3.96g. The N is $\frac{1}{11}$ and the O $\frac{10}{11}$. What is the gas?

(4) A compound of N and H gas weighs .765g to the liter, of which the N is $\frac{1}{4}$. What gas is it.

(5) The analysis of alcohol gives carbon 52.18%, hydrogen 13.04%, oxygen 34.78%. Its v.d. is 23. What is its symbol?

Solution. Every atomic volume of carbon weighs 12, hence there will be as many atomic volumes (and atoms) in 52.18 parts by weight of C as 12 is contained in 52.18. $52.18 \div 12 = 4.35$. The atomic weight of hydrogen is 1, hence there will be $13.04 \div 1 = 13.04$ atomic volumes of hydrogen (and atoms) to every 4.35 of carbon. In the same way ($34.78 \div 16 = 2.17$) the oxygen is 2.17 volumes. Weights have thus been, by use of Avogadro's law, changed to volumes, which now stand, C = 4.35, H = 13.04, O = 2.17. We must now reduce these mixed atomic volumes to whole numbers. This we do by dividing each by the smallest, 2.17, as follows: $4.35 \div 2.17 = 2$ (number carbon atom volumes, or atoms), $13.04 \div 2.17 = 6$ (number hydrogen atom volumes, or atoms), $2.17 \div 2.17 = 1$ (number oxygen atoms). These numbers are not exact, but they should be nearly so. Our symbol is thus C_2H_6O . This is the simplest symbol, and is obtained without the use of vapor density. Is it the correct one, or should the true one be some multiple of it, as $C_4H_{12}O_2$? Computing the v.d. of C_2H_6O from the molecular weight, we obtain 23, which proves it to be correct.

(6) Analysis of a compound gives: C, 26.67%, H, 2.22%, O, 71.11%. What is its simplest symbol? If that is the correct one what should be the v.d. of the substance? Explain all points.

(7) A compound consists of 5.88% hydrogen and 94.12% oxygen. What is its simplest symbol?

(8) An ore of iron analyzes: Fe, 72.41%, O, 27.59%. What is it?

(9) Find the percentage composition of copper nitrate $Cu(NO_3)_2$, and from it compute the symbol again.

Problems very often involve the reduction of weight to volume, or volume to weight, such as the following.

(10) How much phosphorus by weight is contained in 10^1 of PH_3 at N.T.P.? How much volume would the phosphorus occupy in the gaseous state?

Solution. We first find the v.d. from the molecular weight $\frac{31 + 3}{2} = 17$.

The weight of 10^1 will therefore be $17 \times .09 \times 10 = 15.3\text{g}$, of which $\frac{31}{34}$ is phosphorus. The first part is then solved according to Union by Weight, the second by Union by Volume.

$$\begin{array}{rcl} \text{PH}_3 & = & \text{P} + 3\text{H} \\ 34 & = & 31 + 3 \\ \hline 15.3 & = & x + y \end{array} \qquad \begin{array}{l} 34 : 31 :: 15.3 : x \\ x = 13.9\text{g}. \end{array}$$

$$\begin{array}{rcl} \text{PH}_3 & = & \text{P} + 3\text{H} \\ 2 & \frac{1}{2} & 3 \\ 10 & x & y \end{array} \qquad \begin{array}{l} 2 : \frac{1}{2} :: 10 : x \\ x = 2\frac{1}{2}\text{l}. \end{array}$$

(11) A cube of crystallized sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (specific gravity 1.45), is 6cm on a side. (a) How much volume, as a liquid, would the water of crystallization occupy? (b) How much volume the gaseous CO_2 obtainable from the salt at N.T.P.?

Solution. Solve (a) by Union by Weight, computing the weight of the entire block, then find the proportion which the water of crystallization bears to the whole. The number of grams equals the number of cubic centimeters. Solve (b) by ascertaining the weight of Na_2CO_3 in the block, writing an equation for the liberation of CO_2 (say with HCl), then compute the *weight* of CO_2 that can be obtained from the block, and finally reduce this weight to volume, by the use of vapor density and the weight of hydrogen.

(12) How much SO_2 by volume could you obtain by acting with H_2SO_4 on a plate of copper (sp. gr. 8.95) which is $8\text{cm} \times 40\text{cm} \times 44.26\text{cm}$?

(13) How many cubic centimeters of oxygen would it take to burn 75°C of benzene vapor (C_6H_6), and how much volume would the CO_2 formed occupy? Also what would it weigh?

320. Specific Heat. — Every substance has the capacity to absorb heat, but not to the same extent, and experiments

lead to interesting results. If a gram of silver and a gram of iron are heated under like conditions with the same source of heat it is found that to raise the temperature of each a given amount, say 1° , the iron needs to be heated twice as long as the silver, but in raising it 1° it has absorbed twice the quantity of heat which the silver has, and would be twice as long in parting with it. To raise a gram of aluminum 1° would require about 4 times the quantity of heat which the Ag took. A gram of water takes 20 times as much heat as one of Ag. Water has the greatest capacity of any known substance to absorb heat, and hence is made the unit of specific heat.

The specific heat of a substance is the quantity of heat necessary to raise a given weight of that substance 1° , compared to what is necessary to raise the same weight of water 1° . That of water is 1, of other substances is some fraction, e.g., Ag = .056, Fe = .11, Al = .21.

321. Atomic Heat. — In considering the elements it is found that as their atomic weights increase, their specific heats decrease quite regularly, so that *the product of the atomic weight of each solid element by its specific heat is an approximately constant quantity.* For Ag, $107 \times .056 = 5.99$. For Fe, $56 \times .11 = 6.16$. For Al, $27 \times .21 = 5.67$. The average for all solid elements is 6.4. This affords a method of calculating atomic weights. If, e.g., we wish to ascertain the atomic weight of mercury, knowing its specific heat to be .032, we divide 6.4 by .032. $6.4 \div .032 = 200$. Results by this method are not always accurate, but they serve to distinguish between two questionable weights. If it were doubtful whether Hg had an atomic weight of 100 or 200, the specific heat would decide.

The constant 6.4 is called the *atomic heat* of an element, and from this it will be seen that *the heat capacity of all atoms is approximately the same.*

Exercises. — (1) Compute the atomic weight of zinc from the following: (a) 3.27g of zinc produce 4.08g of zinc oxid. (b) 2.18g of zinc, with the required hydrogen chlorid, set free .0665g of hydrogen. (c) The specific heat of zinc is .0955.

Solution. In (a), since we do not know the atomic weight of zinc nor the number of atoms which unite with oxygen, we write the indefinite equation :

$$\begin{array}{r|l|l}
 4.08 - 3.27 = .81 & \text{zinc + oxygen = zinc oxid.} & 3.27 : x :: .81 : 16 \\
 \text{oxygen.} & 3.27x + .81x = 4.08x & .81x = 52.32 \\
 & x \quad 16 & x = 64.7
 \end{array}$$

From the data — supposing that one atom of zinc unites with one of oxygen, and that we know the atomic weight of oxygen to be 16 — the atomic weight of zinc would seem to be 64.7.

$$\begin{array}{r|l|l}
 \text{From (b):} & \text{zinc + } \left\{ \begin{array}{l} \text{hydrogen} \\ \text{chlorid} \end{array} \right\} = \left\{ \begin{array}{l} \text{zinc} \\ \text{chlorid} \end{array} \right\} + \text{hydrogen} \\
 2.18 & 2.18 : x :: .0665 : 1 & .0665 \\
 x & .0665x = 2.18 & 1 \\
 & x = 32.7 &
 \end{array}$$

In the above — assuming that one atom of zinc displaces one of hydrogen — the atomic weight would seem to be 32.7, or about half what (a) gives it. Between these two values the *specific heat* must decide.

(c) Dividing the constant 6.4 by the specific heat of zinc ($6.4 \div .0955 = 67$) proves the first value to be the correct one. In (b) it thus becomes evident that two atoms of hydrogen are set free from the acid by one atom of zinc.

(2) Find the atomic weight of potassium, whose specific heat is .17. (3) Of zinc, with specific heat of .095. (4) Of platinum, with .033. (5) Of lead, with .031. (6) The atomic weight of copper is either 31.5 or 63. Find which is the correct result, its specific heat being .094.

322. Solution Methods. — Several other methods of obtaining molecular weight, based on the properties of substances in solution, have lately been devised. Of these we may mention (1) the *osmotic-pressure* method ; (2) the

boiling-point method ; (3) the *freezing-point* method. Only the last two are at present of practical importance.

323. Osmotic Pressure. — If a porous membrane or a clay cell containing any solution, such, *e.g.*, as sugar or salt in water, is immersed in a vessel filled with the pure solvent, as water (Fig. 145, Chap. XXXI), a gradual diffusion occurs of the dissolved substance outwards and the solvent water inwards. By chemical means it is possible to deposit in the interstices of the porous cell certain precipitates, like copper ferrocyanid, which render its walls impermeable to the passage outward of molecules of the dissolved substance, while allowing molecules of the solvent to pass freely inwards. In such a “semi-permeable cell,” entirely filled with the solution, closed above and immersed in the solvent, it has been found by experiment that particles of the dissolved substance exert an unbalanced outward pressure, which may be measured by inserting a manometer tube in the cell. The liquid will rise in this tube to a maximum which represents the pressure due to the salt. This pressure is called *osmotic pressure*, and is comparable to that exerted by gases. It is often enormous in case of strong solutions.

Pfeffer has shown that the rise of sap in trees is due to osmotic pressure, the cell walls of the plant acting as semi-permeable membranes. Osmotic pressure can be illustrated by the “chemical flower garden,” made by dropping small crystals of colored soluble salts, such as CuSO_4 , NiCl_2 , MnCl_2 , etc., into a strong solution of Na_2SiO_3 or K_2SiO_3 . Films of silicates of the metals are formed which are semi-permeable, and the outward pressure of the salts dissolved within the films, as water passes inward,

causes an upward growth of the salts, not unlike that of plants.

324. Law of Osmotic Pressure. — *The osmotic pressure of a substance in solution in a fixed weight of a given solvent at any given temperature, is proportional to the number of molecules of the dissolved substance, but irrespective of the kind of molecules.*

According to this law — formulated somewhat differently by Van 'tHoff — 342 parts by weight (i.e., one molecular weight) of cane sugar, $C_{12}H_{22}O_{11}$, would produce the same osmotic pressure as 180 parts (one molecular weight) of grape sugar, $C_6H_{12}O_6$. This law is a striking verification of the *molecular theory*, and but for the experimental difficulty in measuring osmotic pressure, it would be a valuable means of obtaining molecular weights.

325. Ions. — The boiling-point of a liquid solvent is raised by the addition of a soluble substance, and the freezing-point of a solvent is lowered by the addition of any soluble substance, in accordance with laws formulated by Raoult, 1886 and subsequently. The boiling and freezing points of liquids can be observed to the .001 of a degree. The application of these laws is most easily made to dilute solutions of organic substances in organic solvents. Very many inorganic salts dissolved, e.g., in water, do not come under the laws. Arrhenius has shown that such salts either do not, in some cases, break up into their molecules, or else, in many other cases, their molecules break up into their positive and negative elements or radicals. $NaCl$, e.g., when dissolved in water, is supposed to break up into a form of $Na + Cl$, and these two exist separately in the solvent. $NaNO_3$ likewise becomes $Na + NO_3$ in solution. These products, Na , Cl , NO_3 , of whose existence there is considerable evidence, are called *ions*, plus or minus, according to whether they are positive or negative.

326. Boiling-Point Law. — *If a substance is dissolved in a fixed weight of a given solvent, the boiling-point of the solvent is raised in proportion to the number of molecules*

of the dissolved substance, but irrespective of the kind of molecules.

327. Freezing-Point Law. — *If a substance is dissolved in a fixed weight of a given solvent, the freezing-point of the solvent is lowered in proportion to the number of molecules of the dissolved substance, but irrespective of the kind of molecules.*

These laws are subject to the exceptions noted above, and can be applied only in dilute solutions. The following case illustrates the laws. One centigram of CS_2 dissolved in 100 grams of acetic acid, raises the boiling-point or lowers the freezing-point of the acid to a degree different from what a centigram of CCl_4 dissolved in it would raise or lower that point, but 76 centigrams (one molecular weight) of CS_2 would raise or lower it to the same extent that 152 centigrams (a molecular weight) of CCl_4 would do. The last law only will be briefly considered.

1. The molecular weight (expressed in grams) of the substance dissolved may be called the *gram molecule*, M ; 76 s is the gram molecule of CS_2 .

2. The depression of the freezing-point made by one gram of a substance in 100 grams of the solvent is called the *coefficient of depression*, C . One gram of CS_2 in 100 grams of acetic acid lowers the freezing-point .505°, which is therefore the coefficient of depression of CS_2 .

3. The depression of the freezing-point of one gram molecule in 100 grams of the solvent may be called the *molecular depression*, D . This is an approximate *constant* for most organic substances in any particular solvent, and is not far from 38.6 for the solvent acetic acid.

From the above it will be seen that $C \times M = D$, or $76 \times .505 = 38.4$, i.e., if one gram of CS_2 made a certain depression, 76 s would produce 76 times as much. It can, however, be used only for dilute solutions.

The coefficient of depression, C , for different weights of the solvent and the dissolved substance is obtained as follows: Let S be the weight of the solvent used, s that of the dissolved substance, and L the lowering of the freezing-point obtained in the experiment. Then $C = L \times \frac{S}{s \times 100}$, for if $S = 100$, and $s = 1$, as in the previous cases, then $C = L$.

Exercises. — (1) Find the molecular weight of propionic acid, from the following: The freezing-point of acetic acid is 16.490°; 0.254 s of

propionic acid with 62.014 $\frac{g}{g}$ of acetic acid froze at 16.277°; the value of D for acetic acid is 38.6.

$$\begin{aligned} \text{Solution.} \quad 16.490^\circ - 16.277 &= .213 = L. \\ 62.014 &= S, \\ 0.254 &= s. \\ D &= 38.6. \end{aligned}$$

$$.213 \times \frac{62.014}{.254 \times 100} = .52 = C.$$

$$38.6 \div .52 = 74.2 = M.$$

(2) The coefficient of depression of a sulfid of carbon in benzene is .654, the molecular depression is 49.7. Find the molecular weight of the sulfid.

(3) The coefficient of depression of chloroform in nitrobenzene is 1.693, and the molecular depression is 69.7. Find the molecular weight of chloroform.

(4) A gram of turpentine, $C_{10}H_{16}$, depresses the freezing-point of acetic acid .288°. Find the molecular depression of turpentine, its molecular weight being 136.

CHAPTER XXVIII.

CONDENSATION AND DIFFUSION OF GASES.

LIQUEFACTION AND SOLIDIFICATION.

328. States of Matter. — Matter exists in three states — solid, liquid, and gaseous. [For the technical definitions of these states students are referred to any work on Physics.] Most if not all solids may, by the application of sufficient heat, be liquefied or vaporized, and all gases, except F,¹ have been liquefied and probably solidified by intense cold and pressure. Some elements, *e.g.*, carbon, have not been liquefied, or even vaporized except at the highest temperature, and many compounds, *e.g.*, ammonium nitrate, are dissociated at a temperature high enough to vaporize them. Water, under one atmosphere (760^{mm}), boils at 100°, though it evaporates at all temperatures. At less than one atmosphere pressure it boils (or vaporizes) below 100°, and under a greater pressure requires a temperature higher than 100°. Such conditions prevail above and below the sea level.

329. Critical Temperature and Pressure. — *Every liquid has a point of temperature and of pressure above which it must pass into the gaseous state, and for every gas there is a certain temperature above which it cannot be liquefied at any pressure.* This temperature is called its critical temperature. The critical temperature of CO₂ is about 31°, and above this point it cannot be reduced to a liquid.

¹ F has since been liquefied by Dewar (1897).

330. History.—Faraday first essayed the liquefaction of gases, and succeeded in the case of eight. Subsequently most gases yielded when subjected to great pressure, though but little attention was given to temperature. Six gases, however, did not yield to this treatment. These were O, H, N, CH₄, CO, NO, and they were called permanent gases. Hydrogen had been subjected to a pressure of 2790 atmospheres and reduced to $\frac{1}{515}$ of its volume without liquefaction. It was finally found that a combination of low temperature and high pressure is necessary to reduce the most refractory gases, and in 1877 the six permanent gases were liquefied by Cailletet and Pictet. There seems to have been some doubt about hydrogen, but in 1895 this gas was liquefied by the Russian chemist Olszewsky, at -233° (about -400° F.). It is doubtful whether this gas has yet been solidified. Moissan, a French chemist, has succeeded in obtaining the highest known temperatures. The measurement of these is attended with much uncertainty, but one metal is said to boil at 1925° (3500° F.), while he obtained as high as 3480° (6300° F.).

331. Low Temperatures are produced by evaporation. The lower the boiling-point of a given substance, the greater the intensity of cold made by its evaporation. Refer to Carré's ice machine, Chap. XVII. By suddenly releasing the pressure from solid nitrogen or air, evaporation

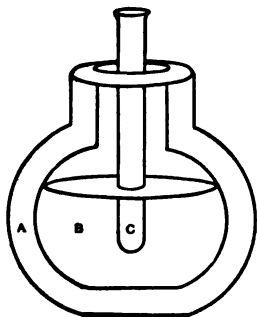


FIG. 118.

tion is so rapid that a very low temperature results. The lowest temperature obtained to the present time, 1897, is about -243.5° (-402° F.). Two sets of indications point to an absolute zero: (1) The action of gases as regards temperature and pressure. (2) The electrical conductivity, as the temperature is lowered, tends to be the same for all metals. Withdrawing

heat deadens matter; *e.g.*, phosphorus will not burn in liquid oxygen.

Air has been solidified by Dewar, as follows: The outer chamber, *A* (Fig. 118), is a vacuum (from which very little heat is absorbed or given off), the next, *B*, has liquid oxygen, from which the pressure is suddenly released, causing it to boil and withdraw heat enough to freeze air in the inner tube, *C*.

Results.—A few results obtained under one atmospheric pressure are:

Boiling-points. C_2H_4 -102° , CH_4 -184° ,
O -180° , N -194° , CO -190° , NO -154° ,
Air -190° .

Freezing-points. Cl -102° , HCl -115° ,
ether -129° , alcohol -130° .

Exp. 186.—Generate SO_2 by heating Cu and H_2SO_4 in a flask, and pass the gas into a U tube, *C* (Fig. 119), which is surrounded by a mixture of ice and salt, *B*. Liquid SO_2 will collect in the bottom of the tube. On removing it, place it in a draft of air for evaporation, and avoid inhaling the gas.

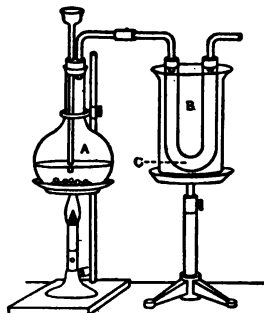


FIG. 119.

DIFFUSION OF GASES.

332. When two or more gases (which do not react upon each other) are put together they gradually intermingle, and finally their molecules become equally distributed throughout the mixture. Molecules of gases are in constant motion, and the lighter the gas the more rapid its motion. It is this motion which gives rise to diffusion. If a receiver of oxygen were inverted over a receiver of carbon dioxide, and left for a time, CO_2 would be found equally distributed in both vessels, and so with oxygen. If a receiver of hydrogen sulfide is opened in a room, the gas is soon detected

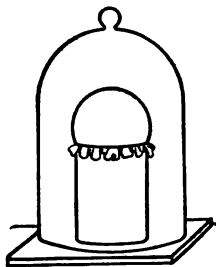


FIG. 120.

all over the room. These may serve as general illustrations of diffusion, as well as the following: Fig. 120 has

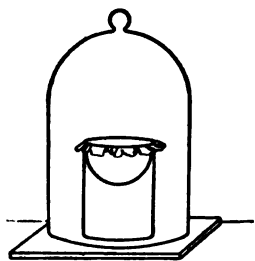


FIG. 121.

the outer receiver filled with hydrogen, the inner with carbon dioxide, the latter being covered with a tightly fitting parchment membrane. Hydrogen passes inward so much more rapidly than the oxide comes out from the inner receiver, through the membrane, that the latter is distended. In Fig. 121, CO_2 is in the outer receiver at first and H in the inner. The case is now reversed, and the membrane is depressed. There is, however, a definite law governing diffusion of gases.

333. History.—Graham investigated the diffusion of different gases, his attention first being called to the rise of water in a cracked jar filled with hydrogen and inverted over water. About 1850 he announced the law of diffusion.

334. Law of Diffusion.—*The diffusibility of gases varies inversely as the square root of their densities.*

According to the law the lighter the gas the more rapidly it diffuses, but only as the square root of its weight. The heavier it is, the more slowly it diffuses. Oxygen is 16 times heavier than hydrogen, hence it diffuses one-fourth as fast; or dif. of $\text{O} : \text{dif. of H} :: \sqrt{1} : \sqrt{16} = 1 : 4$. CO_2 diffuses with oxygen thus: dif. of $\text{CO}_2 : \text{dif. of O} :: \sqrt{16} : \sqrt{22} = 4 : 4.6$, or CO_2 diffuses $\frac{20}{23}$ as fast as O .

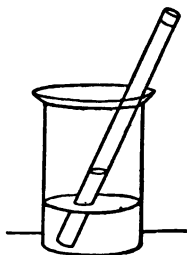


FIG. 122.

Exp. 187.—Seal one end of a tube with some porous material like plaster of Paris, and dry it.

Gases will pass through. Now fill the tube with hydrogen and place it in water (Fig. 122). The hydrogen will gradually diffuse outward through the porous plaster and air will diffuse inward. But the former goes out so much faster than the latter comes in that the water rises in the tube by force of atmospheric pressure. The slow diffusion of heavy gases like CO_2 explains the danger of going into old wells and caves.

Exercises. — Compare the diffusibility of chlorine and N_2O . Of NO_2 and HCl . Of O and N . Of CO_2 and H . Of air and marsh gas, CH_4 . If HCl and NH_3 were put together, would they diffuse? NO and O ? A gas, A , diffuses 3.5 times faster than B . If the molecular weight of A is 4, what is the molecular weight of B ?

CHAPTER XXIX.

SULFUR AND ITS COMPOUNDS.

335. There are three well-marked allotropic forms of this element, as there are of carbon, two of which are crystalline, one being amorphous. Sulfur crystallizes in two different systems, *viz.*, the orthorhombic (Fig. 124) and the monoclinic (Fig. 126). The first is ordinarily obtained by deposit from evaporating a solution of sulfur, the second by cooling from fusion. There are, however, more than thirty different varieties of crystals of sulfur. The amorphous variety is elastic, like rubber, and is obtained by heating melted sulfur to a certain temperature. In this state several of its ordinary solvents do not affect it. Besides the three, there are several other sub-forms which differ more or less from each other. Flowers of sulfur are spherical granules of the element. Sulfur falls with oxygen in the periodic system, and these are the only two elements of that group which we shall study.

336. History. — Sulfur has been known since the early ages. A great deal of importance was attached to it by the alchemists, who thought it was one of two or three primary substances. By the Greeks and Romans it was used as a medicine, and by the phlogistonists was regarded as composed of oil of vitriol and phlogiston. Mitscherlich, early in the nineteenth century, was the first to study its allotropic modifications.

337. Occurrence. — It occurs native and is widely distributed, but not in large amount except in Sicily and

in certain volcanic regions. Up to a recent date most of the supply has come from Sicily, not however in the vicinity of Mt. *Ætna*. Its compounds are more abundant than the element. Many ores, such as those of Pb, Zn, As, Cu, are combinations of metals with sulfur. FeS_2 (pyrite or ferric sulfid) is a very common compound (see H_2SO_4). Sulfates, such as gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, occur in large quantities in the earth, and many other compounds of the element exist. Some mineral springs have solutions of hydrogen sulfid, H_2S . Volcanoes evolve great volumes of S and SO_2 . Sulfur exists in many plants with pungent odor and taste, as mustard, and also often as sulfates, in animals, in eggs, hair, etc. The color of hair is thought to be due in part to organic compounds of sulfur.

338. Preparation.—In Sicily a large admixture of earthy material makes it necessary partially to purify the sulfur before exportation. Loose heaps of the crude sulfur are made, which are covered with earth to prevent the combustion of the entire amount. It is then set on fire, a portion of it burned, and the rest liquefied by the heat. The liquid solidifies, and this product is exported. It is refined and made into *flowers of sulfur* or *roll brimstone* as shown in Fig. 123. The crude sulfur is melted, run into retorts, C, air being excluded, then vaporized and passed into a

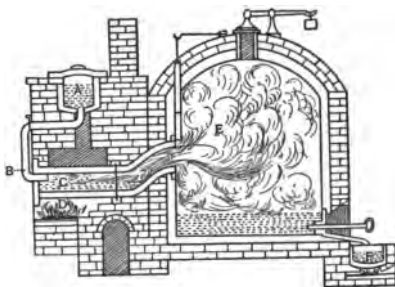


FIG. 123.

chamber, *E*, on the cold walls of which it sublimes as *flowers of sulfur*. As the walls of the chamber become hot, the sublimate melts and the liquid is drawn into moulds. In this form it is called *brimstone*. It is also purified by forcing steam into a mixture of water and sulfur, melting it, and separating it from impurities.

From pyrite it is extracted by heating in a retort from which air is excluded. $3\text{FeS}_2 = \text{Fe}_3\text{S}_4 + 2\text{S}$. Note the similarity of this equation to that for obtaining oxygen from MnO_2 .

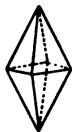
Lac sulfur (milk of sulfur) is obtained by precipitation with HCl from an alkalin solution of a sulfid, a thiosulfate, etc. $(\text{NH}_4)_2\text{S}_2 + 2\text{HCl} = 2\text{NH}_4\text{Cl} + \text{H}_2\text{S} + \text{S}$. The element can be obtained from the CaS in the waste of the soda manufacture (Chap. XXXIII). Sulfates, to be reduced, must first be changed to sulfids, by heating with carbon.

Exp. 188.—Pulverize some FeS_2 in a mortar and place a gram of it in an ignition tube. Heat the tube strongly and observe the phenomena.

Exp. 189.—Into some ammonium polysulfid, $(\text{NH}_4)_2\text{S}_2$, pour a little HCl . Try the action of HCl on sodium thiosulfate solution, $\text{Na}_2\text{S}_2\text{O}_3$.

Exp. 190.—Bring, mouth to mouth—each covered with a glass plate—two receivers, one containing H_2S , the other SO_2 , and remove the plates, allowing the gases to mix.

339. Properties.—*Physical.* Sulfur is a yellow crystal-



line solid, almost white when finely divided, without perceptible odor or taste, not poisonous, but rather healthful in small doses. The so-called sulfur odors come from its compounds, as H_2S , SO_2 , CS_2 , etc. It is insoluble in water, but

carbon disulfid dissolves it without change. From the evaporating solution, crystals of rhombic S (Fig. 124)

form. Some varieties, *e.g.*, *lac* and *amorphous* sulfur, do not dissolve in CS_2 , and the *flowers* only partially dissolve. A globule of *flowers of sulfur* seems to have (Fig. 125) an outside insoluble, or amorphous portion, and an inside one crystalline and soluble in CS_2 . Sulfur melts at



FIG. 125.

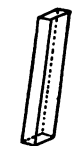


FIG. 126.

115° to a thin, amber-colored liquid; at above 200° it becomes a dark mass so thick as scarcely to be poured; at above 300° it again becomes liquid, but darker than before. If poured into water at the amber stage, it crystallizes, but if at the last stage, it is amorphous and elastic. When allowed to cool from fusion, it crystallizes in the monoclinic system (Figs. 126 and 127). The amorphous and monoclinic forms change, on standing, to the rhombic form, which is the one found in nature. Sulfur boils at 450°, giving a light yellow vapor, which sublimes as flowers of sulfur.

Chemical. Sulfur burns in the air at 260°, forming the dioxid, SO_2 , of characteristic, stifling odor. When moist and finely divided, it will gradually oxidize, combining with O of H_2O . This on exposure to air further oxidizes to H_2SO_4 . $\widehat{\text{O}} + \widehat{\text{SO}}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$. Any common metal, except Al and Cr , when fused with S forms the sulfid. $\text{Fe} + \text{S} = \text{FeS}$. NaOH will dissolve it and form $\text{Na}_2\text{S}_2\text{O}_3$, etc.

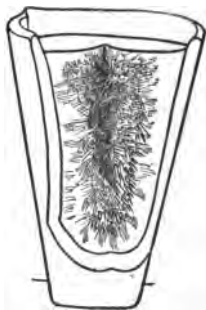


FIG. 127. — Monoclinic sulfur from fusion in a crucible.

Small artificial volcanoes have been made by burying in the earth several pounds of a mixture of iron filings and moistened sulfur. A part

of the iron oxidizes, the rest combines with sulfur, and heat and steam are generated.

Silver spoons are blackened by eggs, because the oil of the egg contains sulfur, which in contact with silver forms the sulfid Ag_2S .

The pigment of hair dyes is Ag_2S , PbS , etc. If sulfur flowers are stirred with water and filtered, the filtrate gives a test for H_2SO_4 .

Exp. 191. — Put into a beaker or test tube 15 or 20* powdered brimstone, and heat *slowly*, noting the phenomena described under "Properties." When it reaches the first or amber stage, cool it. When it begins to solidify on top, pour part of it into some water, and watch the solidification of the rest. Examine that in the water. When it is cool heat the beaker again, and this time carry the experiment through the three stages. When it reaches the third stage, pour some into water, and note the amorphous form and the elasticity. Watch the changes as the beaker cools. To remove the solid S warm it, having a few drops of HNO_3 around the edge.

Exp. 192. — Cover a little powdered brimstone with carbon disulfid, CS_2 , and place the evaporating dish in a draft of air. Watch the action as CS_2 evaporates.

Exp. 193. — Heat a large iron wire red hot, and press a piece of brimstone against it. FeS is formed.

Exp. 194. — Put into a mortar half a gram of a mixture of fine S and KClO_3 , and grind well together. A slight explosion occurs, due to oxidation of the S, similar to the action of KClO_3 and P when a match is scratched.

Exp. 195. — Stir flowers of S with water for some time, then filter, and test the filtrate for H_2SO_4 .

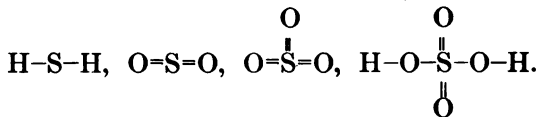
340. Allotropy. — The forms of sulfur furnish a good illustration of allotropy, and serve to give a theory to explain it. Why is it that the forms of sulfur (or of carbon, phosphorus, oxygen, etc.) have properties so diverse from each other, when each form is composed of the same essential element? Chemists suppose that the structure of the molecule is different in one case from that in the other. Possibly it contains more atoms, or those atoms are differently arranged. As a matter of fact sulfur vapor at about 500° has a vapor density of 96, indicating 6 atoms to the molecule, whereas at 1000° its density is 32, giving 2 atoms per molecule. In the solid form we are not sure of the number, but may assume that it is more than the vapor contains, and perhaps the number — or

possibly the arrangement — varies with each allotropic form, and that this number or arrangement explains the different properties. Notice how this may explain the two allotropic states of oxygen.

341. Uses. — Sulfuric acid manufacture consumes a great deal of sulfur, but much of this is now made from pyrite, FeS_2 . Rubber goods and vulcanite contain a small percentage of S. The gum of rubber absorbs the sulfur. Vulcanite is prepared at a higher temperature than rubber. Some of the element is used in forming SO_2 , to bleach straw and woollen goods, and as an antiseptic to destroy the germs of infectious disease, some is used in medicine, some in the laboratory, some for making compounds like FeS and CS_2 , and a great deal for making matches and gunpowder.

HYDROGEN SULFID AND METALLIC SULFIDS.

342. Compounds. — The chief compounds of sulfur are the oxids SO_2 and SO_3 ; sulfids, as H_2S , PbS ; sulfates, as H_2SO_4 , CuSO_4 ; sulfites, as Na_2SO_3 ; and thio-sulfates, as $\text{Na}_2\text{S}_2\text{O}_3$. The element has a valence of 2, 4, or 6. In H_2S and sulfids it is 2, in SO_2 and sulfites 4, in SO_3 and sulfates 6. The following symbols represent the molecular structure :



343. History. — Scheele, 1777, was the first accurate investigator of hydrogen sulfid.

Names. — Hydrogen sulfid, sulfuretted hydrogen, hydrosulfuric acid, sulfhydric acid.

344. Occurrence.— Volcanic gases and certain mineral springs contain the gas, and it is a product of decomposition of organic matter, existing in sewer gas, decayed eggs, etc., to which it imparts its characteristic odor. Sulfids are of common occurrence, since the acid reacts with most metals.

345. Preparation.— Acids acting on sulfids form H_2S . Ferrous sulfid, FeS , and hydrochloric acid, HCl , are commonly used to make the gas for the laboratory. H_2SO_4 might be used, as well as sulfids other than FeS .

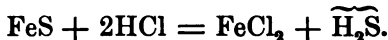


Fig. 128 shows the generator. The gas is passed into water in the second bottle, where it is washed from impurities, and then goes into the solution in the test tube. It can be collected *over* water, though quite soluble, or *in* water. A stream of hydrogen passed through boiling sulfur forms H_2S .

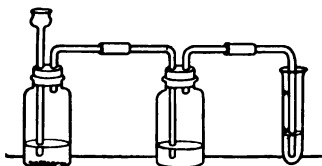
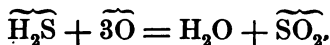


FIG. 128.

Exp. 196.— Put into the first bottle (Fig. 128) 10 or 12 $\frac{1}{2}$ of ferrous sulfid, FeS , add water to seal the thistle tube, and then a little HCl . The second bottle, also the test tube, must contain water.

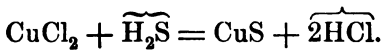
346. Properties.— *Physical.* This is a colorless and transparent gas, but it has an offensive odor somewhat like that of rotten eggs. It is very soluble in water, and its solution is often used instead of the gas. At near 400° it begins to dissociate into its elements, but is not wholly reduced at a very much higher temperature.

Chemical. The gas burns with a blue flame, H_2O and SO_2 being the products.

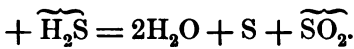


Cold porcelain held in the flame causes a deposit of S. H_2S gas, also a solution of it, oxidizes, forming H_2O and precipitating sulfur.

Most sulfids are insoluble (Table A). These can be prepared from a solution of their salts by adding H_2S , as



A few of these sulfids dissolve in very dilute acid, *e.g.*, in the HCl above, and are not precipitated by H_2S ; hence an alkalin sulfid, $(\text{NH}_4)_2\text{S}$, is the substance used to precipitate sulfids of Fe, Co, Ni, Mn, Zn. H_2S is a reducing agent. Its efficacy is thought to be due to the hydrogen which is so easily liberated. $2\text{FeCl}_3 + \widetilde{\text{H}_2\text{S}} = 2\text{FeCl}_2 + 2\text{HCl} + \text{S}$. It decomposes concentrated H_2SO_4 . H_2SO_4



347. Tests.—Lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, is the best test for H_2S , with which it forms black PbS . AgNO_3 solution answers nearly as well. Sulfids are tested by acting on them with an acid, which liberates H_2S , and this is then tested as above.

Exp. 197.—Try the odor of the gas from a bottle of recently prepared H_2S solution, and test the liquid with litmus. Put a drop of lead acetate solution, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, on paper, and hold it over the mouth of a tube containing H_2S solution, while warming the tube (Fig. 129).

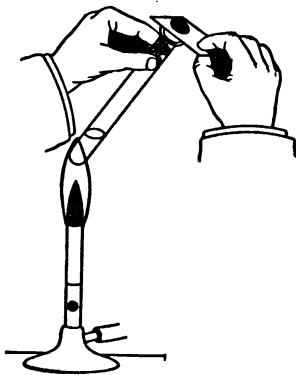


FIG. 129.

Exp. 198.—Put into separate tubes dilute solutions of various salts, *e.g.*, SbCl_3 , CuCl_2 , AlCl_3 , AsCl_3 , and others from Table A. Note in which cases precipitates are obtained, give the colors, and write equations. (Fig. 130.)

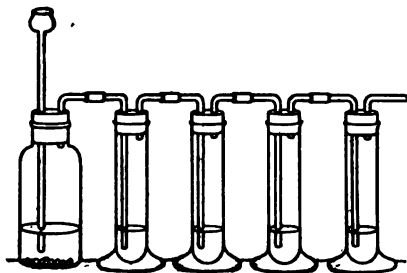


FIG. 130.

Exp. 199.—Make a mixture of solutions of CuCl_2 and AlCl_3 , and try to separate them.

Exp. 200.—Attach a philosopher's lamp tube to a generator of H_2S , and after observing precautions, light the gas. Hold an evaporating dish in the flame for a moment. Also hold the mouth of a clean receiver over the flame. Test any liquid drops with litmus. Rinse the receiver with a little water, and test the latter for H_2SO_4 with BaCl_2 and HCl .

Exp. 201.—Collect a receiver of H_2S by downward displacement, then set the gas on fire and look for any deposit.

Exp. 202.—Heat a little Na_2S with HCl in a test tube, observe any odor, and test the escaping gas with lead acetate paper.

348. Uses.—Hydrogen sulfid is employed chiefly as a reagent in the chemical laboratory, to separate soluble and insoluble sulfids, also to make the latter. Suppose we wished to separate Cu from Ba in a mixture of solutions of the two salts CuCl_2 and BaCl_2 . H_2S is passed into the mixture till no more precipitate, CuS , falls. The barium salt is not precipitated, because BaS is soluble. The solution is then filtered, CuS is left on the filter and the barium salt in the filtrate. A solution of Na_2CO_3 —or other carbonate or sulfate—will precipitate this last salt and take it out of solution.

SULFUR DIOXID.

349. Preparation.—Of the two oxids of sulfur, SO_2 and SO_3 , the former alone is of special importance. The latter is the anhydrid of sulfuric acid, but is seldom prepared, the more common valence of S towards O being 4. SO_2 does not occur native except in volcanic eruptions, fumaroles, etc. It can be prepared by burning sulfur or H_2S in air, or by the reduction of H_2SO_4 , or some sulfate, sulfite, etc. Copper and sulfuric acid heated give the gas. Cu acts as the reducing agent. Other metals would accomplish the same result.



Cu unites with half the SO_4 , all the H combines with enough oxygen to form H_2O , and SO_2 is left.

350. Properties.—It is a gas without color, but it has a very suffocating odor (often erroneously called sulfur odor), is very poisonous, non-combustible, and not a supporter of combustion. It is quite soluble in water, with which it probably combines and forms sulfurous acid, H_2SO_3 , the basis of sulfites (as Na_2SO_3 , which could be made by mixing NaOH with H_2SO_3). This gas can be easily liquefied by passing it through a U tube (Fig. 131) which is immersed in a mixture of ice and salt. The dioxid is a powerful anti-septic and great bleacher.

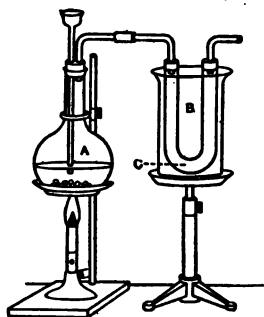


FIG. 131.

A room in which there has been an infectious disease, like scarlet fever, is disinfected by closing it tightly and burning sulfur in it for some time. The SO_2 kills the germs of disease.

Silks, woollens, and straw goods, but not cotton, are bleached by SO_2 .

351. Tests.—The odor, the bleaching action on litmus, etc., and the $\text{K}_2\text{Cr}_2\text{O}_7$ test serve to identify the gas. Potassium dichromate solution (red) is reduced by SO_2 to chromic sulfate, $\text{Cr}_2(\text{SO}_4)_3$ (green). $\text{K}_2\text{Cr}_2\text{O}_7 + 4\widetilde{\text{SO}_2} = \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3$. To test for a sulfite, liberate SO_2 gas from it by the action of an acid, and then test the gas.

Exp. 203.—Place a moist colored rose, green leaf, or blue flower (which bleaches especially well) under a receiver or wide glass jar (Fig. 132), under which also is burning some sulfur in a porcelain crucible.



FIG. 132.

Exp. 204.—Put a drop of potassium dichromate solution, $\text{K}_2\text{Cr}_2\text{O}_7$, on paper, and hold it in a receiver of SO_2 .

Exp. 205.—Shake up some SO_2 gas with blue litmus solution. Try to restore the color with an alkali.

352. Uses.—The dioxid of sulfur is employed in making sulfuric acid, in bleaching, disinfecting, and in preparing certain sulfites. *Sulfates* have been treated of under Sulfuric Acid.

CHAPTER XXX.

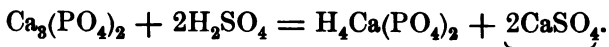
PHOSPHORUS.

353. Without phosphorus it is uncertain how civilized man could live. Previous to the invention of the lucifer match and the chemical tinder, people had either to keep up a perpetual fire or to borrow coals of their nearest neighbors. If there were no compounds of phosphorus to be found on the earth, a very different race of beings must have grown up, for the bones, the brain, and the various tissues of man and the higher animals, contain compounds of phosphorus that have very much to do with life and intelligence. All brain-workers are said to “burn phosphorus.”

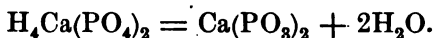
354. History.—Phosphorus was discovered by Brand, a Hamburg alchemist, in 1669, while searching for the philosopher’s stone. He called it *phosphor* (light-bearer), a name previously given to the luminescent sulfid of barium. Scheele, 1775, first described the preparation of the element from bones, and Liebig in 1840 used phosphates as a fertilizer for plants. Romer of Vienna, 1833, first applied phosphorus to matches, and thus revolutionized the means of obtaining fire.

355. Occurrence.—The element is never found in the free state, its affinity for oxygen and other elements being very strong. In compounds it is quite abundant and widely diffused. The principal one of these is calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$. This occurs in certain minerals, as *phosphorite* and *apatite*, in the ashes of bones, in the bone beds of the Southern states, and in guano deposits.

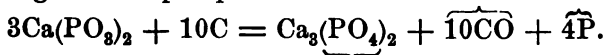
356. Preparation.—The element phosphorus is obtained mainly from bones of vertebrate animals, which usually contain from 55 to 60% of calcium phosphate, (the hard parts of invertebrates being mostly calcium carbonate, CaCO_3). These bones are first either burned or distilled. In either case the ash is the same, but in the latter the carbon is retained as bone-black, which in the former gives rise to carbon dioxid. The volatile substances driven off are ammonia and other nitrogenous products, water, CO_2 , etc. The ash — mostly $\text{Ca}_3(\text{PO}_4)_2$, with a little CaCO_3 — is reduced, and phosphorus obtained by three steps. (1) It is treated with sulfuric acid, which changes it to a soluble phosphate, $\text{H}_4\text{Ca}(\text{PO}_4)_2$.



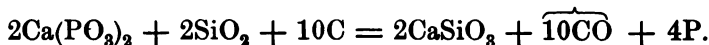
We might expect that H_2SO_4 would change the phosphate salt into phosphoric acid, but the sulfuric used is not very strong and the reaction goes but half way, producing an acid salt. It however changes the insoluble phosphate to a soluble one, and precipitates the calcium sulfate, which is then separated by filtration. (2) The liquid is next evaporated, and the solid residue from the evaporation is strongly heated, a process which breaks it up into calcium metaphosphate, $\text{Ca}(\text{PO}_3)_2$.



(3) The reducing agent carbon, is next added and thoroughly mixed, and heat is again applied, when two-thirds of the phosphorus distills over, the remainder again forming calcium phosphate.



To obtain the whole of the phosphorus, silica, SiO_2 , in the form of sand is introduced and the following takes place:



Great care is taken not to have the phosphorus in contact with air, and retorts are arranged (Fig. 133) so that the phosphorus runs into cold water. The phosphorus must either be redistilled or pressed through chamois skin to get rid of carbon particles, etc. It is then run into small moulds of copper or glass.

Most of the world's supply of phosphorus is made in two places, one in England, one in France, and nearly 3000 tons are produced annually. The process is unhealthful, and dangerous to the workmen. Some of the fumes have to be breathed, and the breath at night is often luminous. The element attacks the teeth and jaw bones, especially the lower jaw, which is sometimes entirely eaten away.

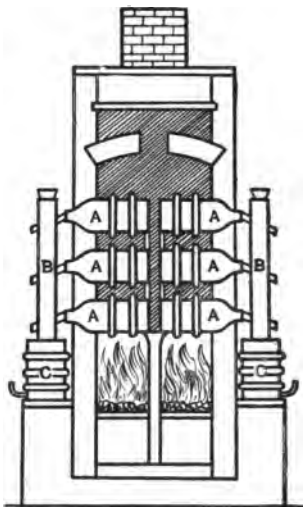


FIG. 133. — A, earthen retorts containing $\text{Ca}(\text{PO}_3)_2 + \text{C}$. The P and CO pass into B, thence into water in C.

357. Properties. — Phosphorus is a yellowish, translucent, crystalline, waxy solid, having a garlic odor, and is very poisonous. It is insoluble in water, but very soluble in carbon disulfid, less so in ether. It slowly oxidizes at a low temperature, and is luminescent in the dark. At 50° it takes fire spontaneously, and if finely divided, at a much lower temperature, forming the pentoxid, P_2O_5 . Slow oxidation gives the trioxid, P_2O_3 . It

should never be handled out of water, in which it is always kept, as it is liable to burn the flesh and also to poison the system. Its burns are very slow to heal, because of the poison absorbed. Phosphorus melts at 44° , boils at 290° . If heated to about 240° in absence of air, it changes to an allotropic, amorphous variety called red phosphorus, but at 300° it changes back. Still another allotropic form, black, crystalline, and metallic, is formed at 530° in a sealed tube free from air. Phosphorus can be made to burn under water. It unites with Cl, Br, I (forming PCl_3 , etc.) with such vigor as to give light. It combines with metals to form phosphids, as Ca_3P_2 . Nitric acid oxidizes phosphorus to H_3PO_4 , orthophosphoric acid.

Red phosphorus differs from the ordinary as shown below.

ORDINARY PHOSPHORUS.

Crystalline.
Very poisonous.
Burns at low temperature.
Phosphorescent.
Soluble in CS_2 .
Garlic odor.

RED PHOSPHORUS.

Amorphous.
Non-poisonous.
Burns only at high temperature.
Non-phosphorescent.
Insoluble in CS_2 .
No odor.

In one property both forms are alike,—they combine with oxygen to form P_2O_5 .

[*Caution.* All experiments with phosphorus must be made with caution, and all the element finally burned, as it is spontaneously combustible.]



FIG. 134.

Exp. 206.—Place a small dry piece of the element in a porcelain capsule resting on a crockery plate. Everything must be perfectly dry. Cover the capsule with a dry and very wide-mouth bottle or beaker. Set fire to the element in the usual way, and cover it (Fig. 134). Note the character of the combustion and the product, and save the latter.

Exp. 207.—Pour a few drops of cold water on the product, P_2O_5 , of the previous experiment. Notice any hissing

sound. Test the liquid with blue litmus. It contains metaphosphoric acid, HPO_3 . $\text{P}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{HPO}_3$.

Exp. 208. — Place a small piece of phosphorus in a test tube, and the latter in a beaker partly filled with *warm* water. Cover the phosphorus with cold water, and let some oxygen from a generator bubble into it. If the oxygen comes in contact with the melted phosphorus, the latter should burn under water.

Exp. 209. — Put on an iron plate, side by side, and at equal distances from a flame at the other end of the iron (Fig. 135), a piece of crystalline and one of amorphous phosphorus. Note the difference in temperature of combustion.

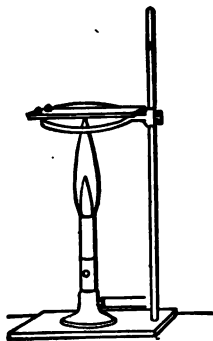


FIG. 135.

Exp. 210. — Pour 5^{cc} of carbon disulfid, CS_2 , into an evaporating dish and drop in a small piece or two of phosphorus. Watch the effect, and soon dip a piece of unglazed paper into the liquid, then hold it in the air till the CS_2 evaporates.

Explanation. — This was evidently a physical solution, phosphorus not seeming to unite with any part of the CS_2 , but the particles of the two substances became thoroughly intermingled, and when the carbon disulfid evaporated, the finely divided particles of phosphorus were in the best state to combine with the oxygen. The paper became covered with a coating of P_2O_5 and was protected from complete combustion.

Exp. 211. — Put a few crystals of KClO_3 into a test tube, add a small piece of phosphorus, and cover the whole with water. Pour on to the KClO_3 , through a thistle tube, a few drops of H_2SO_4 (Fig. 136). Spontaneous combustion under water should ensue. KClO_3 is broken up by H_2SO_4 and imparts oxygen to the phosphorus.

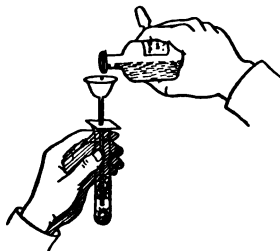


FIG. 136.

Exp. 212. — Into a small flask put a little phosphorus, and cover it with water. Fit to the flask a stopper carrying a short glass tube open at both ends (Fig. 137).

Boil the contents in a dark room. The steam will appear luminous from the minute quantity of phosphorus vapor.

Exp. 213. — Cover lightly with bone-black a small piece of perfectly dry phosphorus and let it stand. Spontaneous combustion may ensue.

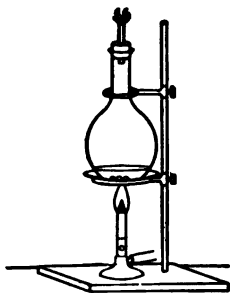


FIG. 137.

358. Luminescence, or Phosphorescence. — If a match is scratched in a dark room a faint line of light is seen as the minute particles of phosphorus which are left glow and oxidize. The same thing occurs if the element is exposed in darkness, and the phenomenon is called phosphorescence. It is due to slow combustion, or oxidation, the product being P_2O_5 . Substances rubbed with phosphorus give the same effect.

Many other minerals and chemical compounds have the power to emit light in darkness, and some of these form the basis of luminous paints. The sulfids of barium, BaS , BaS_2 , BaS_3 , etc., are examples.

Some animals, as fire-flies, glow-worms, etc., emit a light from a certain part of the body, without heat above that of the rest of the body. In Cuba a species of luminescent insect is bottled up and used sometimes for lighting purposes, about 40 of these equaling one candle-power. The light is apparently due to an oxidation of animal tissue which is under control of the insect. To produce the same light by the oxidation of gas or oil, we have a temperature of some $2000^\circ F$, and 99% of the energy of the flame is lost, while these creatures utilize possibly 100% of the energy of oxidation, and without any apparent rise in temperature. The animal supplies its own electric light. On land and on the surface of the sea — as well probably as in the ocean depths — there are millions of micro-organisms which have this power of luminescence. The light rays from decaying fish and vegetable matter are probably due to the same cause. Various forms of phosphorescence have been shown to be due to oxidation on the minutest scale, but there are many other causes of it.

359. Uses. — The element phosphorus is used mostly in the manufacture of matches. A pound of it will tip about a million matches. A little finds use in poison for rats and vermin. Phosphates are made into fertilizers, hypophosphites are prescribed by physicians, acid phosphates

are used as a beverage, and microcosmic salt, $\text{HNaNH}_4\text{PO}_4$, is employed as a flux in the chemical laboratory.

360. Matches. — The making of matches, after the splints are prepared, includes two processes. (1) One end is dipped into melted sulfur, some of which adheres to the wood. (2) It is tipped with a paste consisting of a mixture of phosphorus, an oxidizing agent, and glue. A little coloring matter is often added. The oxidizing agent may be potassium chlorate, KClO_3 (in which case the match snaps and burns vigorously on being scratched), potassium nitrate, KNO_3 , manganese dioxid, MnO_2 , or red lead, Pb_3O_4 . This result is accomplished by pressing the end on a slate slab covered with the paste. Sulfur is necessary, as the heat liberated in the burning of the phosphorus is not enough to set the wood on fire, and a coating of P_2O_5 forms over it. Sometimes paraffin is used instead of sulfur. Safety matches do not contain phosphorus, but instead antimony sulfid, Sb_2S_3 . They are ignited by scratching them on a prepared surface containing red phosphorus, sand, etc. A machine has lately been constructed to cut the splints, tip the matches, and dry and pack them in boxes — all four processes being automatic and continuous, and without poisonous fumes. Over 4,000,000 matches can be made by one machine in a day.

The Chemistry of a Burning Match is quite complicated, but the main parts are easily understood. Friction of the end over a rough surface liberates heat enough to cause the phosphorus to unite with the oxygen of the oxidizing agent in the paste, and cause combustion, the main product of which is P_2O_5 . If the oxidizer is KClO_3 , then KCl is left. The heat of the burning phosphorus is enough to set fire to the sulfur (which unites with the oxygen of the air to form SO_2), and this in turn sets the wood afire. The student should observe everything which

takes place in the burning of a match, and should write as many equations as possible to show all the chemical changes.

361. Acids and Salts.—There are three classes of phosphorus acids, (1) phosphoric, H_3PO_4 , (2) phosphorous, H_3PO_3 , (3) hypophosphorous, H_3PO_2 . These would correspond to the anhydrides P_2O_5 , P_2O_3 , and P_2O , in which the valence of the element is respectively 5, 3, and 1. P_2O , however, probably does not exist. The other anhydrides combine with three molecules of water to form the acids. $3\text{H}_2\text{O} + \text{P}_2\text{O}_5 = 2\text{H}_3\text{PO}_4$. From the *ic* acid are formed the *ate* salts, as H_3PO_4 , Na_3PO_4 (sodium phosphate); from the *ous* acid, the *ite* salts, as H_3PO_3 , Na_3PO_3 (sodium phosphite); and from the *hypo-ous* acid, the *hypo-ite* salt, as Na_2PO_2 , (sodium hypophosphite). It will be seen that these acids are tribasic; hence their hydrogen may be wholly or partially replaced by a metal. Thus there are three salts of H_3PO_4 with Na, (1) Na_3PO_4 (trisodium phosphate), (2) HNa_2PO_4 (disodium phosphate), (3) H_2NaPO_4 (mono or primary sodium phosphate). There are also three classes of phosphoric acids, (1) H_3PO_4 (*orthophosphoric*), (2) $\text{H}_4\text{P}_2\text{O}_7$ (*pyrophosphoric*), (3) HPO_3 (*metaphosphoric*). These may be regarded as derived from the anhydrid, P_2O_5 , by the union of 3 molecules of water, 2 molecules, and 1, respectively.

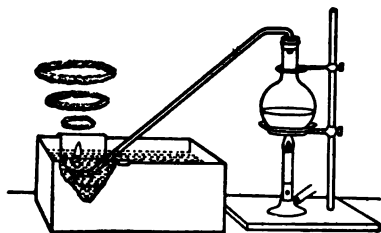


FIG. 138.

with a little ether or with hydrogen, then a piece of phosphorus is introduced and the flask is heated. The delivery tube, as in Fig. 138, extends into water. When PH_3 is formed and escapes into the air it takes fire, and the smoke forms vortex rings.

362. Phosphates.—Wheat contains compounds of phosphorus, and most food plants in order to come to fruitage, must take phosphates from the soil in which they grow. The phosphate must be soluble, so that, as the

Write equations to show this. There are also corresponding salts called orthophosphates, as Na_3PO_4 , pyrophosphates, as $\text{Na}_4\text{P}_2\text{O}_7$, and metaphosphates, as NaPO_3 .

Spontaneous combustion may be well shown by generating PH_3 , phosphin. A strong solution of NaOH or KOH is put into a flask, all the air is expelled

rain dissolves it, it can be absorbed by the rootlet and circulated in the sap of the plant. Soils have to be renewed or fertilized, and most fertilizers contain the soluble phosphate $\text{H}_4\text{Ca}(\text{PO}_4)_2$, made according to the first step in reducing the element. This is transformed and absorbed by the plant, especially the fruit. Animals eat the fruit, and thus the compounds of phosphorus are again transposed, circulated in the system, and deposited wherever needed, as in the bones and nervous tissues. Man feeds upon either plant or animal, and thus obtains his phosphorus. From the human system it is excreted, *via* the kidneys, as phosphates and microcosmic salt, $\text{HNaNH}_4\text{PO}_4$. When the brain is hard worked, more than usual is excreted,—in fact there seems to be a direct ratio between the amount excreted and the vigor of brain action, as though each intellectual effort was attended by the combustion of phosphorus.

It will be recalled that one of the two largest uses of sulfuric acid is in the dissolving of calcium phosphate, and since all soils have ultimately to be renewed, we can see what an enormous industry the fertilizer manufacture is. Not only is phosphorus needed, but nitrogen, potassium, etc., and compounds of these must also be included, such as ammonium compounds, and nitrates of sodium and potassium. The accompanying figure (Fig. 139) may serve to indicate the migrations of a phosphorus atom, as described above, showing that, starting from bone, as insoluble phosphate, it may find its way into plants, fruits, and finally back to the bones of animals. In this way man has been said to "eat his own bones."

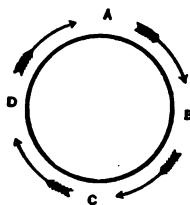


FIG. 139.

363. Tests.—Phosphates, except those of the alkali metals, are insoluble in water, but most are somewhat soluble in dilute HCl . From phosphate solutions (1) AgNO_3 precipitates Ag_3PO_4 (light yellow), soluble in NH_4OH , HNO_3 , or $\text{HC}_2\text{H}_3\text{O}_2$. (2) FeCl_3 throws down yellowish

white FePO_4 , if $\text{NaC}_2\text{H}_3\text{O}_2$ and a little $\text{HC}_2\text{H}_3\text{O}_2$ are first added. The precipitate is dissolved by excess of FeCl_3 . (3) $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH} + \text{MgSO}_4$ precipitate white crystalline NH_4MgPO_4 . (4) $(\text{NH}_4)_2\text{MoO}_4$ throws down yellow $(\text{NH}_4)_3\text{PO}_4(\text{MoO}_3)_3$, if acidified with HNO_3 . This dissolves in excess of the phosphate or in NH_4OH . (5) Heated with a drop of CoCl_2 solution, a phosphate becomes blue.

Exp. 214. — Pour some HNa_2PO_4 solution into a test tube and then add AgNO_3 solution. Divide the precipitate into three parts; try to dissolve one in NH_4OH , another in HNO_3 , a third in $\text{HC}_2\text{H}_3\text{O}_2$.

Exp. 215. — Acidify HNa_2PO_4 solution with $\text{HC}_2\text{H}_3\text{O}_2$, then add a little $\text{NaC}_2\text{H}_3\text{O}_2$ solution, and a few drops of FeCl_3 solution.

Exp. 216. — Pour a little of the following solutions on to HNa_2PO_4 solution in a test tube: NH_4Cl , NH_4OH , MgSO_4 .

Exp. 217. — To a solution of HNa_2PO_4 add a few drops of HNO_3 and then $(\text{NH}_4)_2\text{MoO}_4$. Try to dissolve the precipitate in NH_4OH .

Exp. 218. — Heat B.B.C.C. some $\text{Ca}_3(\text{PO}_4)_2$, and put a drop of CoCl_2 solution on the infusible mass; then heat again.

Exp. 219. — Try to dissolve some $\text{Ca}_3(\text{PO}_4)_2$ in dilute HCl ; filter it, and test the filtrate for a phosphate.

CHAPTER XXXI.

BORON AND SILICON.

BORON.

364. Artificial gems are now usually made from a flint glass to which has been added some boric oxid or acid to produce a glass that is highly refractive to light, and will readily dissolve metallic oxids as coloring matters. The element itself is somewhat like silicon and carbon, the crystalline variety being almost as hard as diamond — according to some authorities harder — and of adamantine lustre.

365. History. — Gay Lussac and Davy independently produced boron, 1808, from boric acid. Wöhler and Deville obtained the crystalline variety, 1856.

366. Occurrence. — It never occurs free, and the principal compounds found are boric acid, H_3BO_3 , and borax

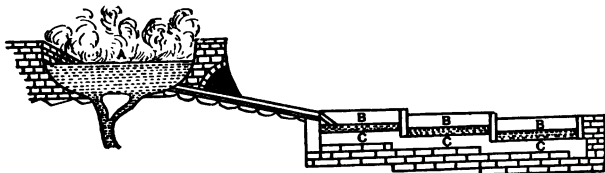


FIG. 140.

(sodium pyroborate), $\text{Na}_2\text{B}_4\text{O}_7$. The former comes from Tuscany, in the volcanic regions of which it issues from fissures in the earth, being brought up in minute quanti-

ties with steam. The steam passes into an artificial reservoir (*A*, Fig. 140), where the acid is condensed in cold water. Half a dozen or more connecting reservoirs, *B*, are built on the side of the hill, each succeeding one lower than the previous. In these the water is partially evaporated at *C*, by the hot gases coming from the earth. It is then drawn off and evaporated further, when the acid crystallizes out. Borax is obtained from Thibet, from Nevada and California.

367. Preparation.—The element can be prepared from the oxid, B_2O_3 , by reducing with potassium. This gives the amorphous variety. The crystalline is obtained by the same operation, but with the addition of Al, which fuses and dissolves it, as zinc dissolves silicon. It is only a cabinet curiosity.

368. Properties.—Amorphous boron is a green-brown powder which burns, forming the only oxid, B_2O_3 . Crystalline boron is extremely hard, transparent, and of adamantine lustre. Boron when heated has very great affinity for nitrogen, forming nitrogen borid, BN. With HNO_3 it forms H_3BO_3 .

369. Compounds.—There are but two important compounds, borax and boric acid. The former has sometimes 10 molecules of water of crystallization, sometimes 5, $Na_2B_4O_7 \cdot 10H_2O$, $Na_2B_4O_7 \cdot 5H_2O$.

Boric acid heated gives B_2O_3 and H_2O . It is a weak acid, turning litmus a wine red and turmeric paper a brown, like an alkali, but on putting a drop of HCl on the paper, it is not turned back to the original color as it would be, had an alkali been used instead of boric acid. This is a test for the acid. The acid also imparts a green color to a flame. A little is used in chemical laboratories, but most of it is made into borax. From the latter it can be made by treatment with HCl.

Borax can also be made from the acid by fusing the latter with sodium carbonate. Its use as a flux depends on its property of dissolving metallic oxids, and thus cleansing the metal. Its use in the laboratory as a test of metals, by the color the metals impart to borax beads, depends on the same property — a clear glass is formed and the metallic compound is dissolved in it, imparting the characteristic color. Some of the applications of borax are in welding to keep the surface free from oxid; in soldering by enamellers and jewelers; in the laboratory by chemists; in artificial gems, in varnish, glass, and soap manufacture, and in medicine.

Exp. 220. — To a strong hot solution of borax in a test tube add some HCl. Let it cool, and keep watch for any crystals. Save the latter, wash them two or three times, then dissolve them in water, and apply the following tests: (1) Test with litmus paper. (2) With turmeric paper, then let it dry, and put on a drop of HCl. Test NH_4OH with turmeric paper, and try this with HCl. Compare the two papers.

Exp. 221. — Pour some of the boric acid solution into a small flask, add some alcohol, shake them well, insert a stopper with a short tube, over which place a wide tube, put the whole over a lamp, and heat the mixture. After a little, set fire to the alcohol, and look for a green flame.

Exp. 222. — Make a loop in a platinum wire (Fig. 141), moisten it, and dip it into powdered borax. Heat it in a flame, and when a clear glass bead is obtained, dip it into a solution of cobalt chlorid, and fuse it again. Observe the blue color.



FIG. 141.

SILICON.

370. As carbon is the central element in the animal and vegetable kingdoms, so is silicon in the mineral world; but unlike carbon, silicon never occurs free. Oxygen

is estimated to make up nearly half of the solid crust of the earth, and silicon to constitute about a third more. These two elements are generally combined in the form of silicon dioxid, or silica, SiO_2 . This non-metallic oxid is often further united with some metallic oxid, such as aluminum oxid, Al_2O_3 , to form a silicate. Hundreds of mineral species are composed of silicates, and the greater number of rocks of the earth's surface are combinations of complex silicates, — limestone, CaCO_3 , being the only important exception. Yet the element itself is separated from its compounds with such great difficulty that it is only a chemical curiosity.

371. History. — Berzelius, in 1810, first separated the element in an impure condition. In 1823 he obtained pure Si. Phipson, in 1864, first reduced it by magnesium.

372. Occurrence. — It does not occur free. Its affinity for oxygen is so great at a high temperature, that in early ages when the earth was a molten mass, the silicon all combined with oxygen to form SiO_2 , this compound later on uniting with metallic oxids to form silicates. Aluminum is the third most abundant element, and so aluminum silicate is the most common of silicates, but there is a great number of others found in every part of the earth. The feldspar of granite is a combination of aluminum and potassium silicates. Mica, hornblende, asbestos, etc., are silicates of varying and complex composition. Granite usually contains from 30% to 40% of silicon.

373. Preparation. — Silicon is never prepared except in very small quantities. This may be done by heating in an iron tube or a Hessian crucible some potassium fluosilicate, K_2SiF_6 , and metallic sodium. $\text{K}_2\text{SiF}_6 + 4\text{Na} = 2\text{KF} + 4\text{NaF} + \text{Si}$. It gives the black amorphous vari-

ety of silicon—left after dissolving out the other two products in water. This variety can be changed to the graphitic by heat. To obtain the transparent variety, zinc is put in with the other ingredients, and as it melts encloses the silicon, which forms in small crystals. When cool the zinc is dissolved by hydrochloric acid. Si can also be reduced by Mg.

374. Properties.—Silicon, like carbon, has three allotropic forms, the amorphous, the graphitic, and the transparent or diamond form. The first combines with oxygen at a high temperature, making SiO_2 , but the crystalline does not combine even at a high temperature. A curious fact is, however, that under these conditions it reacts with carbon dioxid. $\text{Si} + 2\widehat{\text{CO}_2} = \text{SiO}_2 + 2\widehat{\text{CO}}$. Neither do most acids attack crystalline silicon.

375. Oxid.—Unlike carbon, silicon has but one oxid, SiO_2 (though there are two varieties of that, the amorphous and the crystalline). It is commonly called silica or quartz. Rock crystal, flint, jasper, agate are names given to slightly impure, colored varieties of it. Sand is mostly silica, while sandstone and quartzite are composed of sand grains cemented together and metamorphosed. Quartz crystals (Fig. 142) are six-sided prisms terminated by hexagonal pyramids, and are among the hardest of common minerals (ranking 7 in the mineral scale, and scratching glass). They are colorless and transparent if pure, but are often colored with compounds of Fe, Mn, etc., and they have a rounded or conchoidal fracture when broken. Geysers deposit about their mouths amorphous silica in successive layers. The alkaline waters have dissolved the silica in small quantities while it was percolating through the rocks. As the water evaporates, silica is deposited in thin layers. Agate, chalcedony, and opal (each being SiO_2) have likewise been deposited from solutions.

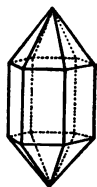


FIG. 142.

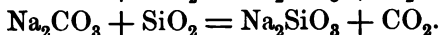
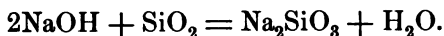
Diatoms (Fig. 143), which in some regions make up large deposits, are the silicious skeletons of minute organisms that have formerly lived in countless millions. The common plant *equisetum* (horse tail), the straw of grains,



FIG. 143 — Diatoms much magnified.

and husks of corn, etc., contain some silica. It imparts strength as well as roughness to their fiber. The horns, feathers, nails, hair, and skin of animals have minute quantities of it. Silica is insoluble in any acid, except hydrofluoric, HF, with which it forms SiF_4 . The amorphous variety, but not the crystalline,

dissolves with heat in solutions of the alkalis or alkalin carbonates. Quartz when pure is infusible, except in the oxy-hydrogen blowpipe, but mixed with metallic oxids it melts at a lower temperature. Both hydrates and carbonates on fusion with silica combine with it to form silicates.



Metallic oxids also, as Na_2O , CaO , PbO , etc., fuse with SiO_2 to form the corresponding silicates. In this way glass is made. SiO_2 is easily prepared from silicic acid by heat, which expels the water, leaving the anhydrid.



The percentage of silica in rocks forms the basis of classification into *acidic* and *basic*. If it contains above

60% of silica, a rock is called acidic, if below 60%, basic.

376. Acids and Salts. — Normal silicic acid is H_4SiO_4 , but this readily parts with half its water, leaving H_2SiO_3 — also called silicic acid. This can be prepared by acting on sodium or potassium silicate (water glass) with HCl . Silicic acid is a thick, gelatinous, white substance, feebly acid, and is the basis of silicates. Besides the ordinary silicates, such as Na_4SiO_4 or Na_2SiO_3 , there are many others more complex, classed as polysilicates, *e.g.*, $\text{Mg}_3\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ — the mineral serpentine. Artificially silicates are commonly made by fusing their constituents, one of which is silicon dioxid, the other may be the metallic oxid, hydrate, carbonate, or sulfate. Soluble glass or water glass, Na_2SiO_3 , is made by fusing SiO_2 and Na_2CO_3 . As found in nature, or as made in art, silicates are not generally simple, but several are combined together, making double silicates, as $\text{H}_8\text{Mg}_5\text{Fe}_7\text{Al}_2\text{Si}_3\text{O}_{18}$ (a species of mica). Fluosilicic acid, H_2SiF_6 , is used for certain chemical tests. The silicates of sodium and potassium are the only soluble ones.

Exp. 223. — Pour into an evaporating dish a few cubic centimeters of water glass (liquid sodium or potassium silicate), and add a little hydrochloric acid. Note the change, then pour off the excess of HCl , and wash the gelatinous mass — silicic acid. $\text{Na}_2\text{SiO}_3 + 2\text{HCl} = 2\text{NaCl} + \text{H}_2\text{SiO}_3$. Press some of it between the fingers. Now heat the residue until it becomes dry, and notice the difference in texture. The acid has been broken up into its anhydrid and water. $\text{Na}_2\text{SiO}_3 = \text{H}_2\text{O} + \text{SiO}_2$.

Exp. 224. — Mix about 10% of powdered fluor spar, CaF_2 , with 20% fine white sand, put them into a flask, and add 40% H_2SO_4 . Have a

large delivery tube run from the flask into water in a receiver (Fig. 144), and dip into some mercury in the bottom, which is contained in a small beaker. The Hg prevents the clogging of the tube by SiO_2 , which is set free as soon as the SiF_4 formed reaches the water. Heat the flask moderately. These reactions take place :

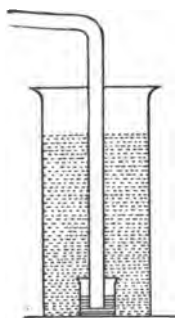


FIG. 144.

(1) $\text{H}_2\text{SO}_4 + \text{CaF}_2 = \text{CaSO}_4 + 2\text{HF}$. (2) $4\text{HF} + \text{SiO}_2 = 2\text{H}_2\text{O} + \text{SiF}_4$. (3) $3\text{SiF}_4 + 2\text{H}_2\text{O} = \text{SiO}_2 + 2\text{H}_2\text{SiF}_6$. The blebs which rise to the surface are pure amorphous silica. Filter through fine muslin, and save the acid and SiO_2 ; dry the latter. H_2SiF_6 is used as a test for sodium and potassium salts, both of which it precipitates. Make several tests, using strong solutions.

Exp. 225.—Try to dissolve in sodium hydrate solution some of the silica obtained in Exp. 224, heating the mixture, if necessary. See whether you can precipitate it with HCl.

377. Dialysis.—Silicic acid furnishes a good illustration of a *colloidal* substance. For convenience substances are classed as *crystalloids* and *colloids*. The former tend to form crystals, the latter jelly-like masses, which do not crystallize. In general colloids will not pass through a membrane of vegetable parchment, while crystalloids will, and this principle is sometimes employed to separate or analyze substances. Formerly it was much used to separate the arsenic, in cases of arsenical poisoning, from the other contents of the stomach. Jelly and caramel are good illustrations of colloids, hydrochloric acid and sodium chlorid of crystalloids. To dialyse substances they are put into a dialyser consisting of a piece of parchment securely fastened to one end of a wide glass vessel, and suspended in water contained in another vessel (Fig. 145). The crystalloid will gradually pass through the membrane into the outer liquid, the colloid will remain behind.

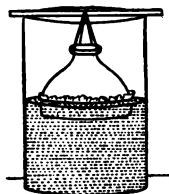


FIG. 145.

Exp. 226.—Make a dialyser by cutting off a wide test tube near the top, and securely fastening to the lip of the tube a piece of parchment, wet in warm water. Put in a solution of potassium iodid and a *very thin* starch paste, and suspend it for a day or two in a receiver with some

water. Finally remove it, and test the water in the receiver with a little chlorin water. If the iodid has gone through the membrane, iodine will be set free. If starch has also passed through, the color should be blue, otherwise not. Starch is a colloid, potassium iodid a crystalloid.

378. Other Compounds.—Si has great affinity for Mg, with which it forms magnesium silicid, Mg_2Si , a little of which put into a beaker and covered with HCl gives the gas SiH_4 . As soon as this gas escapes into the air it ignites spontaneously, like PH_3 , throwing off rings of SiO_2 . (1) $Mg_2Si + 4HCl = 2MgCl_2 + \widetilde{SiH_4}$. (2) $\widetilde{SiH_4} + \widetilde{4O} = SiO_2 + 2H_2O$.

Carborundum (impure SiC), made by passing an electric current through a mixture of powdered charcoal and fine sand, is next to diamond in hardness, and is a valuable abrasive. It crystallizes in flakes, which have a metallic lustre and variegated color.¹

379. Uses.—The element has no special use. Silica has a multitude of mechanical uses, and great quantities go into making the various kinds of glass (including water glass), mortar, etc.

Sodium and potassium silicates act as a cement, and find application in making artificial stone, also in calico-printing, where they are used as mordants, and in soap-making. Kaolin — which is aluminum silicate — feldspar, and silica are fused together to make crockery and china ware, while clay — an impure silicate of aluminum, containing a little potassium and iron silicates — is made into flower pots, jugs, earthen pipes, bricks, etc.

¹ Moissan has just produced a carbid of titanium, said to be harder than the diamond.

CHAPTER XXXII.

GLASS, POTTERY, AND ROCKS.

GLASS.

380. Few manufactured articles are more important than glass. Without it the sciences of physics, chemistry, and all those that employ the microscope or telescope, would make but small progress. Many millions of bottles are made every year, and the uses of glass are almost numberless. In the ateliers of Rome the artists in "stained glass," in making their mosaics distinguish no less than 26,000 different shades of color. The perfection and delicacy in glass-working is nowhere better shown than in the "Blashka glass flowers" at Harvard University.

381. History. — Glass seems to have been made in Egypt as early as 2000 B.C., in very much the same way as we make it, though it was not then clear and transparent, but opaque and variously colored. From Egypt the manufacture spread to Greece and to Rome. The Venetian colored glass of the sixteenth century was famous the world over. There were stained glass windows in Limoges in 979. Porcelain appears to be an early Chinese invention.

382. Kinds and Composition. — Glass is an amorphous mixture of silicates — generally the alkali and alkaline earth silicates. Bottle glass has also aluminum and iron silicates, and flint glass contains silicate of lead. The alkali silicates are amorphous, but the others when cooled from fusion form crystals. The mixture of the two, as found in glass, is amorphous. As usually reckoned there

are four kinds of glass, — (1) window glass, a double silicate of sodium and calcium; (2) Bohemian glass, a double silicate of potassium and calcium; (3) flint glass, a double silicate of potassium and lead; (4) bottle glass, a double silicate of sodium, calcium, aluminum, and iron.

383. Ingredients. — A general symbol for each silicate may be given as follows: Na_2SiO_3 , K_2SiO_3 , CaSiO_3 , PbSiO_3 , $\text{Al}_2(\text{SiO}_3)_3$, FeSiO_3 . A general formula for window glass — not indicating the proportions — would be $x\text{Na}_2\text{SiO}_3 \cdot y\text{CaSiO}_3$. The above statements indicate the general composition of different glasses, but the substances used in making them are very different. Instead of silicates, the compounds put together to be fused are oxids — or such compounds as reduce to oxids by heat, viz., carbonates, hydroxids, etc. Silica, SiO_2 , is always employed. Silica fused with the oxid, carbonate, or hydroxid of calcium forms calcium silicate. Either CaO or SiO_2 alone is almost infusible, but a mixture readily melts.



Write equations for the others. Flint glass — so named because powdered flints were formerly used for the silica — employs an oxid of lead, PbO or Pb_3O_4 , for the base. The first three glasses require very pure materials, but not so with bottle glass, the ingredients of which may have such compounds as alumina, Al_2O_3 , oxid of iron, FeO , etc. Granite — consisting of feldspar and quartz — is sometimes used for the SiO_2 in bottle glass, and the green color of bottles is due to ferrous silicate. A red-brown color indicates ferric silicate. An illustration of the proportion of ingredients going to make up flint glass, which the student can weigh and put into test tubes, is as follows: SiO_2 10 parts, Pb_3O_4 2 parts, K_2CO_3 4 parts, cullet 7.5 parts.

384. Manufacture. — Pure white sand is mixed with the metallic oxids required, in the proportion which experience has shown gives the best results, and some old glass — called *cullet* — is added to improve the quality. The mixture is put into the pots (Fig. 146).



FIG. 146.

These are made of the most refractory fire clay, and are

placed in a circular furnace (Fig. 147) with openings

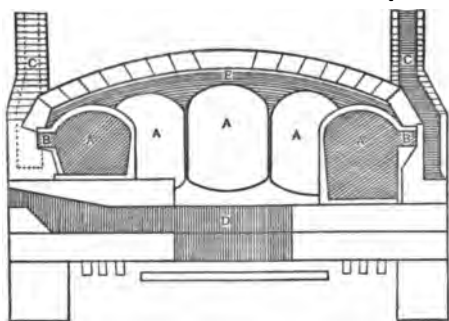


FIG. 147. — Circular glass furnace. *A*, fire-clay pots; *B*, openings for introducing blowpipe; *C*, chimney; *D*, source of heat; *E*, roof, whence heat is reflected downward.

through which the workman can dip his long iron blowpipe into the pots. The fuel now used is mostly gaseous, and an intense heat is kept up for hours, till the substances are completely fused and mixed. The glass-worker dips his

blowpipe — a hollow iron rod 5 or 6 feet long — into the fused mass, removes a small portion, rolls it on a smooth iron surface, swings it round in the air, blowing meanwhile through the rod, cuts it with shears, curves and bends it at will, welds it, etc., and thus fashions it as desired into flasks, lamp shades, etc. The accompanying illustration, Fig. 148, shows the making of a goblet. For such uses as bottles the glass is run into moulds; for others, as flasks, it is blown; for still other kinds it is rolled, as in window glass. Glass objects, in order not to break easily, must be annealed, or cooled slowly, so that the molecules may arrange themselves in a natural way. This is accomplished by putting them on a very slowly moving slide in a long chamber, one end of which is heated strongly, the temperature gradually diminishing to the other end, where it is cool. Glass is toughened by dipping when very hot into hot oil. Cut glass is finished at great expense by subsequent grinding on emery wheels,

etc. Glass may be made semi-opaque by etching with a

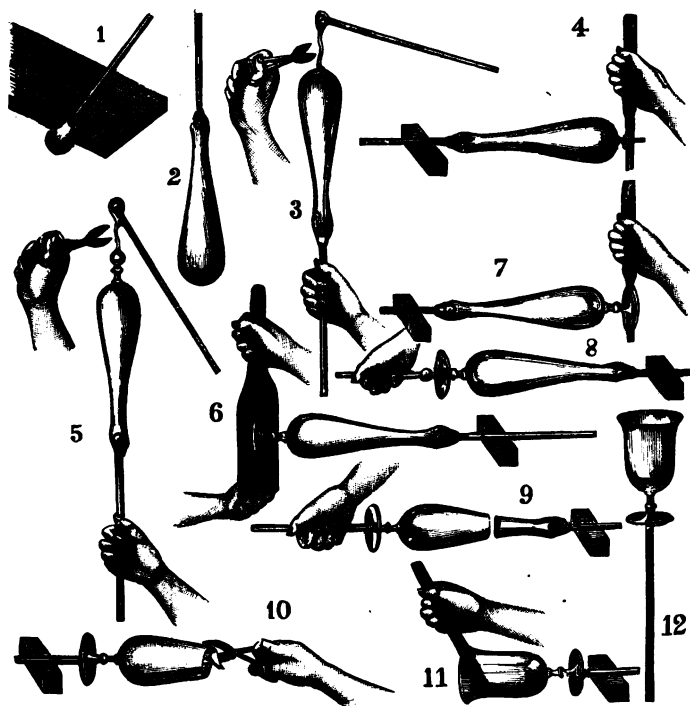


FIG. 148. — Making a goblet. 1, pellet of glass on blowpipe; 2, after having been blown; 3, 5, pieces welded on for base; 4, 6, 7, 8, finishing base; 9, 10, cutting off top; 11, finishing top; 12, complete goblet.

blast of sand, or with hydrofluoric acid. Designs are etched on glassware with HF.

Exp. 227. — Make a mixture of equal parts of sodium carbonate and potassium carbonate — enough for a platinum wire bead (Fig. 149). Use the blowpipe, and when a clear bead is obtained dip it into powdered silica, and fuse it with *continued blowing till the bead is transparent*.

Glass is thus formed, i.e., a double silicate of sodium and potassium.



FIG. 149.

This may be colored by dipping it into a dilute solution of cobalt chlorid, and again fusing.

385. Color and Opacity. — If colored glass is desired, mineral pigments, usually oxids, are added to the mixture before fusing. If, however, a superficial color is wanted, it can be subsequently painted on to the ware, and then baked. This is often done with chinaware. To impart a blue color to glass, smalt—a silicate of cobalt made from cobalt oxid, CoO , and glass—is used. Uranium oxid, U_3O_8 , gives a beautiful yellow, cupric salts give a deep green, cuprous a pure red. The “purple of Cassius” is furnished by mixing chlorids of gold and tin, AuCl_3 and SnCl_2 . Glass is apt to have a green tint caused by a little iron. MnO_2 in small amounts is used to correct this tint. Opacity or enamel, such as many lamp shades have, is produced by adding to the mixture As_4O_6 , Sb_2O_3 , SnO_2 , cryolite, etc.

PORCELAIN AND POTTERY.

386. Making and Glazing. — Genuine porcelain and chinaware are manufactured from a fine white clay called kaolin — $\text{Al}_2(\text{SiO}_3)_2$, resulting from the disintegration of feldspathic rocks — and silica. After being fashioned, the porcelain is “fired,” then glazed and re-fired. One mode of glazing consists in dipping the object into a powder of feldspar and silica suspended in vinegar, and then fusing. Jugs, drain-pipes, and coarse earthenware are glazed by volatilizing NaCl in an oven which holds the porous material. The glaze goes into the pores of the ware, with which it partially combines to form sodium and aluminum silicates. If on being heated, the ware and glaze expand uniformly, the glaze does not crack. Flower-pots and other porous pottery are clay that has been moulded

and baked, but not glazed. Bricks are baked clay. The green color of ordinary clay is due to iron salts in the ferrous state; the red of bricks shows that baking has oxidized ferrous to ferric iron, FeSiO_3 to $\text{Fe}_2(\text{SiO}_3)_3$. Some clay, having no iron, is white. Such is mainly kaolin, $\text{Al}_2(\text{SiO}_3)_3$, and is infusible, being on this account used for fire bricks, clay pipes, etc. The more silica a clay contains, the more infusible it is, and the more iron, the more fusible it is. Calcium oxid or graphite is, however, more refractory than either clay or silica.

387. Properties and Uses.—(1) Window glass may be regarded as the type of ordinary glass. Its use is in windows, mirrors, etc. (2) Bohemian glass is a very tough refractory variety, employed for such chemical apparatus as ignition tubes, flasks, etc., because it will not melt at a high temperature. (3) From flint glass are made the lenses used in optical instruments, and cut glassware, which have a high refractive (not refractory) power. This melts at a low temperature, and is hence called soft glass. The refractive power of two glasses may be shown by Fig. 150, in which *A* represents a lens of window glass that refracts light less than *B*, one of flint glass. In *B* the rays come to a focus nearer the lens than they do in *A*. Spectacles, eyeglasses, etc., are a flint glass which is called *crystal glass*. Most of this is made in a single town in France. *Strass*—from which artificial or paste gems are made—is of the same, but has more lead oxid and a little boric acid, H_3BO_3 . The sparkle of gems is due to their high refractive power.

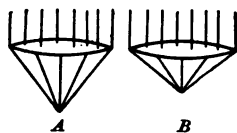


FIG. 150.

ROCKS.

388. Composition. — Most rocks of the earth's crust are siliceous, hence the abundance of compounds of silicon. Slate and schist are mixed silicates, and sandstone is mostly SiO_2 . Obsidian — of which a mountain transparent as glass exists in Yellowstone park — is a glassy silicate. Limestone, CaCO_3 , is the only extensive rock from which silica is absent. Silicates of aluminum, iron, calcium, potassium, sodium, and magnesium are most common, and these metals rank in abundance next to oxygen and silicon. Rocks are not usually definite compounds, but variable mixtures of minerals. Minerals — of which some 1500 varieties are now known — may be simple substances, as graphite and sulfur, or definite chemical compounds, as galena and gypsum. Granite rock is composed of two essential minerals — feldspar and quartz — and usually one or more accessory ones, as mica or hornblende. Quartz when pure is SiO_2 ; feldspar — one variety — is a double silicate of aluminum and potassium. The complexity of these silicates is shown by the following symbol of one variety of mica — $\text{H}_8\text{Mg}_5\text{Fe}_7\text{Al}_2\text{SiO}_{18}$.

389. Soils and Earth. — Beds of sand, clay, etc., are disintegrated rock. Sand is chiefly SiO_2 ; clay is decomposed feldspar, slate, etc. Soils are composed of these with an added portion of carbonaceous matter from decaying vegetation, which imparts a dark color. The reddish-brown hue so often observed in rocks and soils results from ferric compounds.

390. The Earth's Interior. — We do not know how far down siliceous rocks extend, for we are ignorant of the chemistry of the earth's

interior. The deepest borings are but little more than a mile, and volcanic ejections probably come from but a very few miles below the surface. These are in part siliceous. The specific gravity of the interior is known to be more than twice that of the surface rock. From this it has been imagined that towards the center heavy metals like iron and gold predominate; but this is by no means certain, since the greater pressure at the interior would cause the specific gravity of any substance to increase.

391. Bunsen's Analysis. — From extensive analyses of granitic rocks — which are representative siliceous rocks — Bunsen estimated the chief elements in the earth's crust to be as follows :

O	44 — 48.7%	Ca	6.6 — 0.9%
Si	22.8 — 36.2%	Mg	2.7 — 0.1%
Al	9.9 — 6.1%	Na	2.4 — 2.5%
Fe	9.9 — 2.4%	K	1.7 — 3.1%

More than half the elements are known to exist in sea water, and it is imagined the others may be there, though in such minute quantities as to elude detection.

CHAPTER XXXIII.

METALS AND ALLOYS—ALKALI METALS.

METALS AND ALLOYS.

392. Metals and Non-Metals.—The majority of elements are metals, only about a dozen being non-metallic in their properties. The division line between the two classes is not very well defined; *e.g.*, arsenic has certain properties which ally it to metals, but others which are non-metallic. Hydrogen occupies a place between the two classes. The following are the more marked characteristics of each group:

METALS.

1. Metals are solid at ordinary temperatures, and usually of high specific gravity.

Exceptions: Hg is liquid above -39.5° ; Li is the lightest solid known; Na and K will float on water.

2. Metals reflect light in a manner peculiar to themselves. They have what is called a metallic lustre.

3. They are white or gray.

Exceptions: Au, Ca, Sr are yellow; Cu is red.

NON-METALS.

1. Non-metals are either gaseous or solid at ordinary temperatures, and of low specific gravity.

Exceptions: Br is a liquid; I has the heaviest known vapor.

2. Non-metallic solids have different lustres, as glassy, resinous, silky, etc.

Exceptions: I, B, and C have metallic lustre.

3. Non-metals have no characteristic color.

4. In general they conduct heat and electricity well.

5. They are usually malleable and ductile. Exceptions, As, Sb, Bi.

6. They form alloys, or "chemical mixtures," with one another, similar to other solutions.

Exceptions: Some, as Pb and Zn, will not alloy with one another.

7. Metals are electro-positive elements, and unite with O and H to form bases.

Exceptions: Some of the less electro-positive metals, with a large quantity of O, form acids, as Cr, As, etc.

Numbers 2, 6, and 7 are the most characteristic and important properties.

4. They are non-conductors of heat and electricity.

Exceptions: C and some others are conductors.

5. They are deficient in malleability and ductility.

6. They often form liquid solutions, similar to alloys in metals.

7. Non-metals are electro-negative, and with H, or with H and O, form acids.

393. Oxidizers and Reducers. — An oxidizer (or oxidizing agent) is a substance which will raise the valence of a metal or positive part of a compound. See also page 51. Nitric acid or chlorin will change ferrous to ferric salts; hence HNO_3 or Cl is an oxidizer. A reducer (or reducing agent) is a substance which will lower the valence of a metal (or positive part of a compound). Nascent hydrogen (*i.e.*, hydrogen just set free from a compound, and in the atomic state) changes ferric to ferrous salts; hence hydrogen is a reducer. In general, metals are reducers, and many non-metals are oxidizers. The following are a few oxidizers employed in the laboratory, sometimes with heat, sometimes without: oxygen, ozone, chlorin, bro-

min, chlorates, nitrates, peroxids. These are reducers : carbon, hydrogen, zinc and other metals, stannous chlorid.

394. Alloys. An alloy is not usually a definite chemical compound, but rather a mixture of two or more metals which are melted together. One metal may be said to dissolve in the other, as sugar dissolves in water. The alloy has, however, different properties from those of its elements. For example, plumber's solder melts at a lower temperature than either Pb or Sn, of which it is composed. Some metals can alloy in any proportions. Solder may have two parts of Sn to one of Pb, two of Pb to one of Sn, or equal parts of each, or the two elements may alloy in other proportions. Not all metals can be thus fused together ; *e.g.*, Zn and Pb do not alloy. Nickel, silver and gold coins are alloyed with Cu.

Gun metal, bell metal, and speculum metal are each alloys of Cu and Sn. Speculum metal, used for reflectors in telescopes, has relatively more Sn than either of the others ; gun metal has the least. An alloy of Sb and Pb is employed for type metal, as it expands at the instant of solidification. Pewter is composed of Sn and Pb ; brass, of Cu and Zn ; German silver, of brass and Ni ; bronze, of Cu, Sn, and Zn ; aluminium bronze, of Cu and Al.

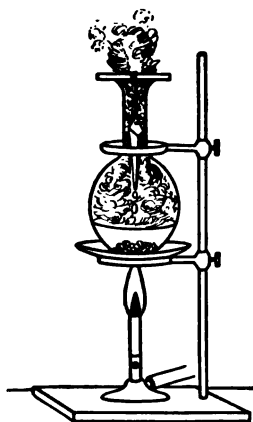


FIG. 151.

Low fusibility is a property of many alloys. Wood's metal, composed of Pb 8 parts, Bi 15, Sn 4, Cd 3, melts at just above 60° , or far below the boiling-point of water, whereas Pb alone fuses at 326° , Bi at 268° , Sn at 233° , and Cd at 320° . Fig. 151 shows this alloy melting in steam.

By varying the proportions of elements different fusing-points are obtained. This principle is applied in automatic fire alarms, and in safety plugs for boilers.

and fire-extinguishers. Water pipes extend along the ceiling of a building and are fitted with plugs of some fusible alloy, at short distances apart. When, in case of fire, the heat becomes sufficiently intense, these plugs melt and the water flows out.

395. Amalgams. — An amalgam is an alloy of Hg and another metal. Mirrors are sometimes “silvered” with an amalgam of Sn. Tin-foil is spread on a smooth surface and covered with Hg, on which the glass is pressed.

Various amalgams are employed for filling teeth, a common one being composed of Hg, Ag, and Sn. Au or Ag, with Hg, forms an amalgam used for plating. Articles of gold and silver should never be brought in contact with Hg. If a thin amalgam cover the surface of a gold ring or coin, Hg can be removed with HNO_3 , as Au is not attacked by it. Heat will also quickly cause Hg to evaporate from Au.

Exp. 228. — Pour into a dry mortar a drop of mercury the size of a pea. Cut a piece of sodium half the size into pieces as large as a pin head — first removing the naphtha with blotting-paper — then drop them one by one into the mercury, and press the two elements together with a pestle. This forms sodium amalgam. It is decomposed by water.

Exp. 229. — Cautiously pour on the sodium amalgam (Exp. 228) in a test tube a little of a very strong solution of NH_4Cl . Ammonium amalgam is formed, which swells to some 20 times the former volume, but rapidly decomposes into NH_3 , H, and Hg.

396. Ores. — An *ore* of a metal is either the metal itself or some compound of it which is dug from the earth and yields the metal sufficiently pure to pay for production. The compounds are often oxids or sulfids, carbonates, sulfates, etc. Gold and platinum, and often copper, occur free. Ores are mixed with earthy

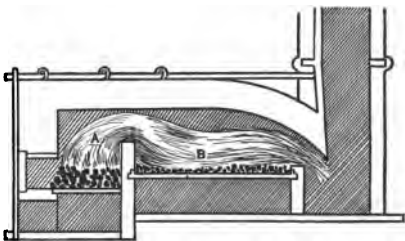


FIG. 152.

material called *gangue*. Ores are often reduced in reverberatory furnaces, which consist of two compartments, one of which, *A* (Fig. 152), contains the burning fuel, the heat and flame from this being reflected downward from the low roof of the furnace on to the ore in the other compartment, *B*.

397. Arrangement. — The metals will be taken up in the following order, which very nearly corresponds to the classification for analysis: The alkalis; alkaline earths; Co, Ni, Mn, Zn; Fe, Cr, Al; As, Sb, Sn; Bi, Cd, Cu; Ag, Pb, Hg, Au, Pt. This seems better than to follow rigidly the order of the periodic law.

THE ALKALI METALS.

398. An alkali is a very soluble, caustic base. The three common alkalis are hydrates of potassium, sodium, and ammonium. By reference to Chap. IX it is seen that potassium and sodium are the most metallic or positive of the metals, hence they form the strongest bases. Ammonium, NH_4 , though a radical existing only in compounds, reacts so like a metal that it is commonly regarded as one. The metals potassium and sodium are very like in appearance and reactions, and their compounds have also great similarity. The naturally occurring salts of sodium — especially the chlorid — are far more abundant than those of potassium.

399. History. — Davy in 1807 obtained K and Na by electrolysis of the hydrates. Before that time KOH and NaOH were regarded as elements.

400. Occurrence. — By reason of their properties, these elements can exist only in compounds. Of these silicates are the most abundant. Double silicates of sodium or potassium with aluminum and other metals

are very widespread in such minerals as feldspars, micas, etc. The chlorids and nitrates are the next most important native compounds. NaCl occurs in sea water, of which it constitutes about three



FIG. 153. — Formation of cubical crystals of NaCl from solution.

per cent ; in salt lakes, whose waters sometimes

hold thirty per cent or are nearly saturated ; and as rock salt, called *halite*, in large underground masses. Poland has a salt area of 10,000 square miles, in some parts of which the rock salt is a quarter of a mile thick. In Spain there is a mountain of salt five hundred feet high and three miles in circumference. In New York and Michigan



FIG. 154. — NaCl crystallized from solution.

NaCl is obtained by evaporating the brine of salt wells, either by fire or the sun's heat. (Figs. 153, 154 show formation of crystals from solution.) In Poland NaCl is mined like coal. In southern France it is obtained by evaporating sea water, which at high tide flows into shallow basins ; and in Norway

and Siberia it is separated by freezing sea water, a process which concentrates the solution, as salt is excluded from freezing water, and ice is fresh. Potassium chlorid, KCl, called *sylvite*, is found in quantity only in one locality, Stassfurt, Germany. *Carnallite*, KMgCl_3 , is also known. Sodium nitrate, or Chile saltpetre, NaNO_3 , is found mainly in Chile, and potassium nitrate, or nitre, KNO_3 , much less abundantly in India and the warm countries of the East. Both are made by the action of micro-organisms on decomposing organic matter.

401. Reduction. — Both metals are now obtained from their carbonates by the reducing agency of heat and carbon, CO being liberated. An intimate mixture of the carbonate and powdered charcoal is made, placed in a retort, *A*, (Fig. 155) that is connected with an iron receiver, *B*, from which air is excluded. Strong heat is applied, and the metal vaporizes and distills over into the receiver, from which it is then passed into petroleum, or an oil containing no oxygen or water.

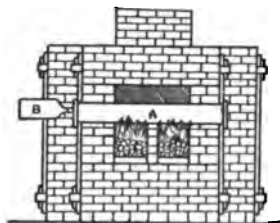


FIG. 155.

The process is difficult and delicate ; hence the high price of the metals.

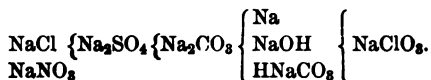
402. Properties. — Both K and Na are white metals with a brilliant metallic lustre, of so small specific gravity that they float on water, which, however, they decompose rapidly, forming KOH and NaOH and liberating hydrogen (Fig. 156). This action is so vigorous, and so much heat is set free in the case of potassium, that both hydrogen and potassium are set on fire. To produce the same effect with sodium, hot water must be used. The metals are always kept under naphtha (a liquid containing no water or oxygen). On exposure, both oxidize rapidly to K_2O and Na_2O , and assume a dull lustre. These oxids dissolve in water to form hydroxids. Both potassium and sodium are energetic reducing agents and decompose many very stable compounds. Carbon is set free by them from CO_2 , and aluminum, silicon, etc., from their compounds, especially the chlorids, as K or Na has marked affinity for Cl.



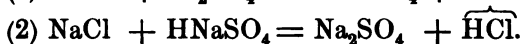
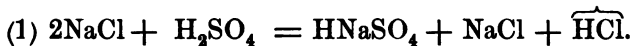
FIG. 156.

403. Compounds. — Some of the more important compounds of sodium are shown in the following table, which also shows the compound

from which each is prepared. The table should be committed to memory. A corresponding table would represent the compounds of potassium.



404. Sodium Sulfate. — This salt is made by the action of H_2SO_4 on NaCl . Moderate heat applied to the acid and salt mixture gives the acid salt, HNaSO_4 . A higher temperature produces the normal salt, Na_2SO_4 . Both reactions liberate HCl .



Twice as much NaCl as will combine at the moderate temperature is first mixed with the acid in the iron pan,

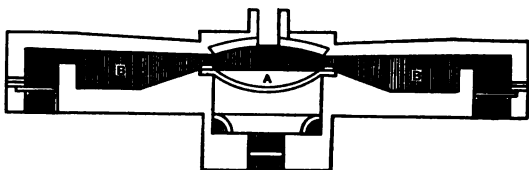


FIG. 157.

A (Fig. 157), when reaction (1) takes place. Finally the mixed products, HNaSO_4 and NaCl , are raked into the hotter parts, *B*, of the reverberatory furnace, and reaction (2) takes place. HCl gas is collected in towers through which water falls, is dissolved in the water, and drawn off at the base. Great quantities of the sulfate are made, mainly as a step in the sodium carbonate manufacture. It crystallizes with $10\text{H}_2\text{O}$, is very efflorescent, and is often called *Glauber's salt*. It is used also in glass-making, in the laboratory, and in medicine.

405. Sodium Carbonate.— This is made by two processes, the *Le Blanc* and the *Solvay*. For a century the *Le Blanc* process has been in use. It consists in changing Na_2SO_4 to Na_2CO_3 . As a carbonate does not

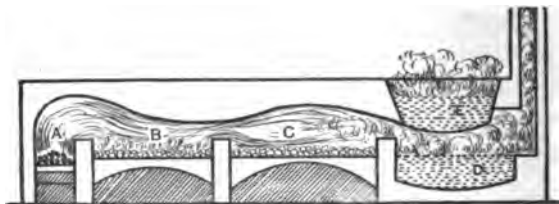


FIG. 158.

break up a sulfate, the process cannot be direct. The Na_2SO_4 is first reduced to Na_2S by action of heated carbon. The product Na_2S is then acted on by that most abundant of carbonates, CaCO_3 , with heat. Practically the two reagents are thoroughly mixed with the Na_2SO_4 at the same time, so that the two reactions are simultaneous. The mixture is put into the coolest part, *C*, of the reverberatory furnace, Fig. 158. Afterwards it is pushed along to the hotter part, *B*, where the reaction is completed. $\text{Na}_2\text{SO}_4 + 4\text{C} = \text{Na}_2\text{S} + 4\text{CO}$. $\text{Na}_2\text{S} + \text{CaCO}_3 = \text{CaS} + \text{Na}_2\text{CO}_3$. The two products CaS and Na_2CO_3 (blackened by carbon) are called *black ash*. Na_2CO_3 , being very soluble, is separated from CaS , which is insoluble, by water, from which the carbonate is obtained by evaporation at *D* and *E*. The waste product CaS contains the original sulfur in the sulfuric acid. It can now be broken up and the sulfur used again.

406. The Solvay Process (or ammonia process) is more economical, but it gives no muriatic acid. It is of recent discovery, and

consists in making the carbonate from NaCl solution by the action of ammonia and carbon dioxide. Fig. 159 illustrates the process on an experimental scale. In the Wolff bottle is put a saturated solution of NaCl in H_2O . One flask is a CO_2 generator, containing $CaCO_3$ and HCl. The other is an NH_3 generator, containing either NH_4OH or $Ca(OH)_2$ and NH_4Cl . CO_2 and NH_4OH combine in the Wolff bottle and form first $(NH_4)_2CO_3$, then HNH_4CO_3 . (1) $2NH_4OH + \widehat{CO_2}$

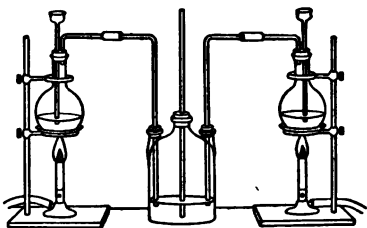


FIG. 159.

$= (NH_4)_2CO_3 + H_2O$. + (2) $(NH_4)_2CO_3 + \widehat{CO_2} + H_2O = 2HNH_4CO_3$. Bicarbonate of ammonium now reacts with sodium chloride to form bicarbonate of sodium, which, being rather insoluble, is precipitated. $HNH_4CO_3 + NaCl = \underbrace{HNaCO_3}_{\text{precipitate}} + NH_4Cl$. On filtering and heating the $HNaCO_3$, there is formed the normal carbonate. $2HNaCO_3 = Na_2CO_3 + H_2O + \widehat{CO_2}$. The CO_2 can be used over again, and the NH_4Cl is mixed with $Ca(OH)_2$ and made again into NH_4OH . Immense quantities of Na_2CO_3 are used in glass manufacture and in the preparation of other compounds of sodium.

407. Sodium Bicarbonate.—This substance, called also primary sodium carbonate, acid carbonate, etc., is made by passing CO_2 into a strong solution of Na_2CO_3 (v. $H_2Ca(CO_3)_2$, Chap. XXI), and is used in bread-making to liberate CO_2 . It is an excellent antidote for acidity of the stomach. This and the corresponding potassium salt, $HKCO_3$, are known as *saleratus*. $K_2CO_3 + H_2O + CO_2 = 2HKCO_3$.

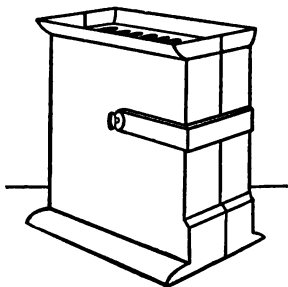


FIG. 160.

408. Hydroxids.—The preparation and uses of these are described in Chap. XVIII. $Na_2CO_3 + Ca(OH)_2 = \underbrace{CaCO_3}_{\text{precipitate}} + 2NaOH$. KOH or NaOH is melted and run into cylindrical moulds (Fig. 160).

409. Chlorates.—Potassium chlorate, $KClO_3$, is the more important of the chlorates. It is made from calcium chlorate, $Ca(ClO_3)_2$, the

latter being produced from milk of lime, $\text{Ca}(\text{OH})_2$, and chlorin as follows :

$2\text{Ca}(\text{OH})_2 + 4\widehat{\text{Cl}} = \text{Ca}(\text{ClO})_2 + \text{CaCl}_2 + 2\text{H}_2\text{O}$. The hypochlorite of calcium, $\text{Ca}(\text{ClO})_2$, thus formed is changed by heat into calcium chlorate. $3\text{Ca}(\text{ClO})_2 = \text{Ca}(\text{ClO}_3)_2 + 2\text{CaCl}_2$. This chlorate reacts with KCl to form KClO_3 . $\text{Ca}(\text{ClO}_3)_2 + 2\text{KCl} = 2\text{KClO}_3 + \text{CaCl}_2$. Potassium chlorate is used as an oxidizing agent in the laboratory, and also as a medicine.

410. Potassium Cyanid.—This is one of the most poisonous of chemical substances. It has the symbol KCN , is the source of hydrocyanic acid, HCN , also a deadly poison, is employed in medicine, also as a solvent of silver chlorid and as an insecticide.

411. Gunpowder.—Gunpowder is an intimate mechanical mixture of carbon, sulfur, and saltpetre, KNO_3 . Heat or concussion causes violent chemical action, changing the solids into several gases, as CO_2 and nitrogen, which at the moment of explosion occupy some 1500 times their original volume. The equation $2\text{KNO}_3 + \text{S} + 3\text{C} = \text{K}_2\text{S} + 2\widehat{\text{N}} + 3\widehat{\text{CO}_2}$ may represent approximately the reaction of an explosion. Gunpowder is made from fine charcoal, pure saltpetre and distilled sulfur, which are mixed in a revolving drum, then made into a paste with water and put under great pressure. It is afterwards granulated, sifted to separate the coarse and fine grains, and glazed by revolving in a drum with a little powdered graphite.

Exp. 230.—Pulverize separately and mix intimately on paper 5s KNO_3 , 1s S , 1s charcoal. Pile the mixture on a brick, and set it on fire.

412. Ammonium.—This is the radical NH_4 , and is too unstable to exist alone, but it forms salts similar to those of other alkali metals. Ammonium compounds, such as NH_4Cl , NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, NH_4OH , $(\text{NH}_4)_2\text{CO}_3$, etc., are derived mainly from the destructive distillation of soft coal in gas works. They are of use in the laboratory, and also as a constituent of fertilizers, for the nitrogen which they furnish to plants. Decaying organic matter, vegetable and animal, forms NH_3 and its compounds.

413. Tests.—All the common compounds of sodium, potassium, and ammonium are soluble; hence the metals are easily separated from others. In analysis they are classed as one group and are separately

tested for. Compounds of sodium color the flame orange-red, of potassium pink or purple. The spectroscopic test (see *Physics*) serves also to distinguish them. PtCl_4 solution precipitates K_2PtCl_6 and $(\text{NH}_4)_2\text{PtCl}_6$ from their respective salts, but does not affect sodium salts. Fluosilicic acid with a *strong* solution of Na or K salts gives a precipitate, but not with NH_4 . Nessler's solution gives a brown precipitate of $\text{NHg}_2\text{I} \cdot \text{H}_2\text{O}$ with NH_4 salts. NH_3 is also liberated from NH_4 compounds by NaOH , KOH , or $\text{Ca}(\text{OH})_2$ (Chap. XVII). Experiments in Chaps. XVII, XVIII, and V on these metals and their compounds should be reviewed.

Exp. 231. — Test solutions of chlorids of each of the three metals by adding a drop of PtCl_4 solution.

Exp. 232. — Test each with H_2SiF_6 , also with Nessler's solution. The latter will give a precipitate if the slightest trace of ammonia is present.

Exp. 233. — Apply the flame test by dipping a Pt wire into the solution and then holding it in the outer edge of a Bunsen flame.

Exp. 234. — Test solutions of these salts with HCl , H_2S , NH_4OH , $(\text{NH}_4)_2\text{S}$, $(\text{NH}_4)_2\text{CO}_3$, and note whether a precipitate is formed.

CHAPTER XXXIV.

THE ALKALIN EARTHS.

BARIUM, STRONTIUM, CALCIUM, MAGNESIUM.

414. The elements of this group — barium, strontium, calcium, magnesium — form a connecting link between alkali metals and other metals. Their hydrates are all somewhat soluble, but not as much so as those of the alkalis. The metals themselves, except magnesium, are only cabinet curiosities, and are very difficult to obtain from compounds. The compounds of calcium are extremely abundant in the earth, and of magnesium considerably so, while those of barium are much less often found, and of strontium rather rare. Lime is obtained from calcium carbonate, and plaster of Paris from calcium sulfate. Marble is a variety of crystallized CaCO_3 . These elements, then, are mainly important in their compounds. The flame of burning magnesium is rich in actinic rays, and hence is employed in flash-light photography.

415. History. — Scheele, in 1774, first distinguished lime, CaO , from baryta, BaO . It was not until 1808 that Davy isolated all the alkaline earth metals by electrolysis.

416. Occurrence. — The chief naturally occurring compounds of these four elements are carbonates and sulfates, as follows: barite, BaSO_4 , witherite, BaCO_3 ;

strontianite, SrCO_3 , celestite, SrSO_4 ; calcite, CaCO_3 , selenite or gypsum, CaSO_4 ; magnesite, MgCO_3 , dolomite, $\text{MgCa}(\text{CO}_3)_2$. Silicates of magnesium (serpentine, talc, etc.) are abundant, and silicates and phosphates of calcium are found. These ores are widely distributed. The limestone in the earth is said to contain 300 times the amount of CO_2 which the coal in the earth, if burned, would form. The greatest quantity of celestite comes from Sicily, whence thousands of tons are annually exported. It occurs there with sulfur and gypsum. *Epsom salt* is MgSO_4 . It exists in water in certain mineral springs.

417. Reduction.—Each element of this group may be reduced either by electrolysis, or by heating the chlorid with sodium or potassium. That it is a difficult process is shown by the fact that calcium is quoted at \$10 a gram (\$5000 per pound).

418. Properties and Compounds.—Barium, strontium, and calcium are all yellow metals, readily fusible. They oxidize in the air, and rapidly decompose water with formation of hydrogen and hydroxids. Magnesium is white, it slowly oxidizes, but does not decompose water unless heated. It burns in air with a dazzling white light, forming white amorphous MgO . Each metal is usually a dyad. The oxids BaO , SrO , CaO , MgO can be made by heating the nitrates, oxalates, carbonates, or hydroxids. The most important of these is CaO , quicklime, made by heating CaCO_3 with carbon, in kilns, carbon being used to produce heat. $\text{CaCO}_3 = \text{CaO} + \widetilde{\text{CO}_2}$. All the mortar of brick buildings and the interior plastering of houses consists in large part of lime. Mortar is made by slaking lime and mixing it with sand

and water. Slaking changes CaO to Ca(OH)_2 , which with water and sand makes a cement that hardens or "sets," and slowly combines with CO_2 of the air, forming CaCO_3 , at the same time adhering to the SiO_2 of the sand and silicates of brick or stone. The mortars of walls hundreds or thousands of years old are more strongly adhesive than when first applied. The sand should be clean, coarse, and sharply angular, and four or five times the volume of lime.

Hydraulic lime contains a large percentage of silica and alumina, and it hardens under water.

CaO strongly heated gives a great light, as does any infusible substance. This is employed, with the oxy-hydrogen flame, for the Drummond or calcium light. Lime water, consisting of Ca(OH)_2 dissolved in water, is a test for CO_2 (see Chap. XXI). Milk or cream of lime consists of Ca(OH)_2 suspended in water. Ca(OH)_2 is also used in making the alkalis and bleaching powder, in tanning skins, purifying gas, etc.

The dioxid BaO_2 — prepared by oxidizing BaO with KClO_3 , etc. — is used in the making of hydrogen dioxid, H_2O_2 . MgO , magnesia, finds some application in medicine.

The soluble salts of these metals are best made by dissolving their carbonates in the requisite acid. Write several equations. From what other compounds could they be obtained? Many of them have — under certain conditions — water of crystallization, as $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Certain compounds of these metals very well illustrate relative solubility. BaSO_4 — one of the most insoluble of substances — will dissolve in some 800,000 parts of water, SrSO_4 in 7000, CaSO_4 in 400.

and MgSO_4 in 3 parts. The hydrates dissolve as follows : $\text{Ba}(\text{OH})_2$ in 20 parts, $\text{Sr}(\text{OH})_2$ 60, $\text{Ca}(\text{OH})_2$ 700, $\text{Mg}(\text{OH})_2$ 55,000 parts. CaCl_2 is used by chemists for drying gases, as it has great affinity for water. The salts of barium impart a green color to a flame, those of strontium a crimson, of calcium a yellowish red. Nitrates and chlorids of the first two metals are used in pyrotechny for green and red fires.

BaSO_4 is used to adulterate white lead in paint, and is called *permanent white*. In the laboratory it serves to determine sulfates quantitatively.

Plaster of Paris, CaSO_4 , is obtained by heating gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and expelling the water. If not too strongly heated, the CaSO_4 on being mixed with water takes again $2\text{H}_2\text{O}$, and very soon sets, forming a hard, amorphous mass. Hence its very great use for taking *plaster casts* of objects. MgSO_4 is a medicine. *Calcium phosphate*, $\text{Ca}_3(\text{PO}_4)_2$, is described in Chap. XXX.

The sulfids of these elements, particularly the polysulfids of barium, have a curious phosphorescent property, and are used as the basis of phosphorescent paint. They seem to absorb light, then to give it out in darkness. The cause of this phenomenon is uncertain, but on account of it the compounds were known as *Bononian phosphorus*. The sulfids are obtained by reducing the sulfates with heated carbon. They are soluble, and from them the other salts are made.

Bleaching powder, CaCl_2O — made by causing chlorin to act on lime — is employed as a bleacher and disinfectant. On exposing the bleaching powder to the air, Cl is slowly liberated and destroys odors and germs. Its bleaching action is described in Chap. XXVI.

419. Tests and Separations.—Ba, Sr, Ca are precipitated together as carbonates by $(\text{NH}_4)_2\text{CO}_3$. Mg is held in solution, and thus separated, by NH_4Cl . It is then precipitated in the filtrate as white NH_4MgPO_4 , by adding NH_4OH and HNa_2PO_4 . The three precipitated carbonates are next dissolved in acetic acid, from which Ba is removed as yellow BaCrO_4 by $(\text{NH}_4)_2\text{CrO}_4$, or $\text{K}_2\text{Cr}_2\text{O}_7$. Strontium is precipitated as white SrSO_4 by $(\text{NH}_4)_2\text{SO}_4$, and calcium oxalate is the white precipitate obtained by adding $(\text{NH}_4)_2\text{C}_2\text{O}_4$ to the filtrate.

The flame tests named above serve in a measure to distinguish the salts. The carbonates and oxalates of Ba, Sr, Ca are all white and insoluble. The chromate of Ba is insoluble, of Sr is soluble, if with acetic acid, and of Ca is soluble. From the solubilities of the sulfates (see above), how could you test for Ba with SrSO_4 , for Sr with CaSO_4 , and for Ca with MgSO_4 ?

Exp. 235.—To separate solutions of BaCl_2 , SrCl_2 , CaCl_2 , MgCl_2 , add MgSO_4 solution. Repeat the experiment with CaSO_4 solution, then with SrSO_4 . Explain each result.

Exp. 236.—To separate solutions of BaCl_2 , SrCl_2 , CaCl_2 , MgCl_2 , add acetic acid, then $\text{K}_2\text{Cr}_2\text{O}_7$ solution.

Exp. 237.—Try the flame tests—using a platinum wire—for Ba, Sr, Ca, from their chlorids.

Exp. 238.—To a mixture of all the above chlorid solutions add NH_4Cl solution, NH_4OH , $(\text{NH}_4)_2\text{CO}_3$ solution. Filter, and add to the filtrate HNa_2PO_4 solution. Dissolve the precipitate in $\text{HC}_2\text{H}_3\text{O}_2$, and add $(\text{NH}_4)_2\text{CrO}_4$, then filter. Add to the filtrate $(\text{NH}_4)_2\text{CO}_3$, and filter. Dissolve the precipitate in $\text{HC}_2\text{H}_3\text{O}_2$, dilute it, and add $(\text{NH}_4)_2\text{SO}_4$ solution. Filter, and add to the filtrate $(\text{NH}_4)_2\text{C}_2\text{O}_4$. Interpret each result from the statements above.

Exp. 239.—Test separate solutions of the above salts with HCl , H_2S , NH_4OH , $(\text{NH}_4)_2\text{S}$. Test MgCl_2 solution with NH_4Cl solution, and then add NH_4OH .

420. Hard Water.—Water is hard when it will not give a lather with soap. The hardness is usually due to salts of Ca or Mg—the carbonates or sulfates—dissolved in the water. Soap, which is chemically sodium stearate, palmitate, etc., dissolves in pure water, and the faintly alkaline solution very readily gives *emulsions* with the skin or

fatty matters in soiled cloth, and thus mechanically removes any dirt. Now if soluble salts of Ca or Mg are present, a stearate of these metals—a lime or magnesium soap—is formed and precipitated. Hence no soap can dissolve till all those salts are removed. Waters of temporary hardness contain CaCO_3 or MgCO_3 in solution, probably in the form $\text{H}_2\text{Ca}(\text{CO}_3)_2$, or $\text{H}_2\text{Mg}(\text{CO}_3)_2$. These bicarbonates are described in Chap. XXI. The water can be softened by boiling, which liberates CO_2 and precipitates CaCO_3 . Spring water in limestone countries is always hard. Permanently hard water contains CaSO_4 , MgSO_4 , etc., in solution, and cannot be softened by boiling. Na_2CO_3 added to such water tends to soften it, as CaCO_3 and MgCO_3 are precipitated. The quantity of soap solution necessary to make a lather is the basis for estimating the hardness of water.

Exp. 240.—Dissolve a shaving of soap in 10 or 12^{cc} of water in a test tube, warming the latter. Pour some into three tubes, one of which contains distilled (or soft) water, another a solution of MgSO_4 , a third some lime water which has had CO_2 passed into it until it is clear. Shake each of the tubes, and note the result.

Exp. 241.—Pass CO_2 into lime water till the precipitate clears, then boil it for some time, and filter. To the filtrate add soap solution, and shake it.

CHAPTER XXXV.

NICKEL, COBALT, MANGANESE, ZINC.

NICKEL.

421. Within a few years the production of this element has greatly increased, owing to its extensive use as an alloy of certain kinds of steel, in the plating of iron and other metals, and in the smaller coins of most countries. Our five-cent coin contains 75% Cu, 25% Ni; the one-cent coin 88% Cu, 12% Ni. Nickel comes into the market in the form of small cubes or of grains. The metal itself is white, and does not readily tarnish. Its salts are green in color.

422. History. — The element was discovered by a German named Cronstedt, in 1751, in the mineral niccolite.

423. Occurrence. — Its ores are not widespread or abundant. New Caledonia produces *garnierite* (hydrous silicate of Ni, etc.), and Saxony, Ontario, and the United States produce it as *niccolite*, NiAs, and as a by-product of *pyrrhotite*, Fe_7S_8 . Nickel is an important constituent of meteorites, in which it exists uncombined. In the earth its ores are in the older geologic rocks.

424. Reduction. — The ore is roasted, then heated with carbon or hydrogen, as in the case of cobalt. To obtain it chemically pure the oxalate, NiC_2O_4 , is heated with

hydrogen. The commercial cubes are made by precipitating $\text{Ni}(\text{OH})_2$ by $\text{Ca}(\text{OH})_2$ from a solution of its salts, then igniting the product to NiO , which, with powdered charcoal, is pressed into cubes, and then heated.

425. Properties and Compounds. — Nickel is a white metal, ranking in hardness second only to manganese, and is capable of taking a high polish. It is malleable and ductile, and is magnetic if cold, but not when heated. It alloys with most metals, does not oxidize in the air, nor is it much affected by H_2S or CO_2 . It fuses at 1420° — about the same temperature as iron. When molten it absorbs gases and on cooling gives them up, as silver does. Like pig iron it contracts as it cools. It is not volatile, except in the electric furnace — in which, indeed, all metals volatilize. Nickel easily dissolves in HNO_3 and very slowly in HCl or H_2SO_4 . In plating, the double sulfate of Ni and NH_4 is employed. The element is a dyad (very rarely a triad). Its most important salts are $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, each of which is green in color. They are generally made by dissolving NiO in the respective acids. NiS is prepared by adding $(\text{NH}_4)_2\text{S}$ to a soluble Ni salt, since H_2S does not precipitate it from acid solution — except from solutions of salts of weak acids, like acetic.

426. Tests and Separations. — In the oxidizing flame with the borax bead, nickel salts give a brown-violet color when hot and yellow when cool, and in the reducing flame a gray color, both hot and cold. Even a trace of cobalt obscures the color. Most reactions of Ni and Co salts are similar, but the metals may be separated as follows: add solutions of tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, then NaOH till it is alkaline, finally H_2S , and boil it, when CoS precipitates. NiS is formed, but is held in solution by NaSH and forms a dark liquid. The reactions are as follows:

(1) $\text{NiCl}_2 + \text{H}_2\text{C}_4\text{H}_4\text{O}_6 = \text{NiC}_4\text{H}_4\text{O}_6 + 2\text{HCl}$; (2) $\text{NiC}_4\text{H}_4\text{O}_6 + 2\text{NaOH} = \text{Ni}(\text{OH})_2 + \text{Na}_2\text{C}_4\text{H}_4\text{O}_6$; (3) $\text{Ni}(\text{OH})_2 + \text{H}_2\text{S} = \text{NiS} + 2\text{H}_2\text{O}$; (4) $\text{NaOH} + \text{H}_2\text{S} = \text{NaSH} + \text{H}_2\text{O}$. In (1) nickel tartrate is held in solution by tartaric acid, and in (3) the NiS is held in solution by NaSH in (4). The same reactions apply to cobalt, but NaSH does not hold CoS in solution.

Co and Ni may also be separated by adding acetic acid, then potassium nitrite solution, NaNO_2 , which precipitates the former as potassium cobaltic nitrite, $\text{K}_3\text{Co}_2(\text{NO}_2)_{12}$, complete after several hours. $2\text{CoCl}_2 + 10\text{KNO}_2 + 4\text{HNO}_3 = \text{K}_3\text{Co}_2(\text{NO}_2)_{12} + 2\text{H}_2\text{O} + 4\text{KCl} + 2\text{NO}$. Both Ni and Co are separated from Mn and Zn by the solubility of the sulfids of the two latter in dilute HCl, and the insolubility of those of the two former except in *aqua regia*, or hot concentrated HCl.

Exp. 242. — Take solutions of NiCl_2 in three test tubes. To one add a few drops of NH_4OH , and to a second a little HCl. Pass H_2S into each of the three and note the results. Take a fresh solution of NiCl_2 in three clean tubes, and treat two as before with NH_4OH and HCl, then add to all $(\text{NH}_4)_2\text{S}$. Explain the results.

Exp. 243. — Add $(\text{NH}_4)_2\text{S}$ to a mixture of solutions of NiCl_2 and CoCl_2 . After filtering, dissolve the precipitate in *aqua regia*, evaporate the free acid, add $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ solution, then NaOH solution till the liquid is alkaline, then saturate it with H_2S and boil it. The precipitate is CoS, and NiS is in solution.

Exp. 244. — To a mixed solution of NiCl_2 and CoCl_2 add $\text{HC}_2\text{H}_3\text{O}_2$, then NaNO_2 solution. Let it stand for several hours, then filter and add NaOH solution to the filtrate. Explain the result from the text above.

Exp. 245. — Make a borax bead and fuse into it a solution of a nickel salt first in the outer flame, then in the inner, noting the colors of each bead when hot and when cold.

427. Uses. — Nickel is used in alloys such as German silver (Ni, Cu, Zn), with steel, and other metals, and in the lesser coins, in crucibles and dishes for the laboratory, weldings upon iron and steel plates, culinary utensils, and in plating on iron and other metals. Its alloy with steel is now of much importance.

COBALT.

428. History. — The name *cobalt* originally meant a goblin which was supposed to haunt mines. It also meant a false mineral. The alchemists used the term with no idea of the element. Compounds of cobalt, under the name of *smalt*, are now used to color glass a deep blue. Some Egyptian glass is found colored with smalt, but modern use of the pigment dates from the sixteenth century. The element was probably discovered by Brandt about 1735.

429. Occurrence. — Cobalt does not occur free, but is usually combined with sulfur and arsenic and associated with nickel, being not abundant nor widely diffused. It is found in Pennsylvania and Missouri, in Germany, and in other places, and often in meteorites. The two chief minerals are *smaltite* (Co, Fe, Ni) As_2 , and *cobaltite*, $CoAsS$.

430. Reduction. — The ores are roasted and melted in a blast furnace which in part removes the S and As. The residue is then dissolved in HCl and other impurities are removed. A solution of $Ca(ClO)_2$ then precipitates $Co(OH)_3$, which by heat is converted into Co_2O_3 . Co_2O_3 is ignited and a current of hydrogen passed over it. This forms metallic cobalt.

In the laboratory it can be prepared by igniting the oxalate, CoC_2O_4 , in a crucible, the air being kept out by powdered glass, or it may be obtained from the oxid by heating with Na, K, or C.

431. Properties. — It is a white metal with a slightly reddish tinge, harder than iron, and is malleable. Most of its properties are almost identical with those of nickel. In a powder it absorbs oxygen, often igniting spontaneously. It does not change at usual temperatures, but slowly oxidizes when heated, and burns with a red flame. It is magnetic, and soluble in HNO_3 . It forms no alloys of importance and has no use as a metal.

432. Salts. — Co has a valence of 2 or 3, only the *ous* salts being important. Cobaltous salts are usually either red (if hydrated) or blue (if anhydrous). The oxid, CoO , is the chief but not the only commercial compound. The chlorid, $CoCl_2$, and nitrate, $Co(NO_3)_2$, are used in the laboratory and are made from the oxid, carbonate, or hydrate. Give the equations. Very concentrated solutions of the salts are blue. Weaker solutions may be made blue by boiling. Ordinary solutions when cold are some shade of red.

433. Sympathetic Ink. — An aqueous solution of a cobalt salt forms a sympathetic ink, the writing of which is invisible unless heated, when it can be easily read. Heat is supposed to expel the water, leaving the blue anhydrous salt, which on cooling resumes its water. This ink may have its color varied by addition of other salts, as Fe'' (green), Zn (red), Cu (yellow). "Floral hygrometers," or weather-indicators which are pink in damp weather and blue in dry, consist of tissue paper sensitized with cobalt salts.

Exp. 246. — Make a solution of the chlorid or nitrate and write with it on paper. When it is dry examine the writing, then heat it. Mix also some of the above coloring solutions and test the result in writing.

434. Smalt. — The main use of cobalt is in the blue pigment *smalt*, used for coloring glass and porcelain. Smalt is a finely powdered potash glass intensely colored by CoO . A little of it added to molten glass colors it a beautiful and permanent blue. It is made in Saxony.

435. Tests. — The tests and separations are given under Nickel. The blue color imparted to a borax bead serves as a test for Co salts.

Exp. 247. — Dip a borax bead into a weak solution of CoCl_2 and heat it again with the blowpipe.

Exp. 248. — To a solution of CoCl_2 add a little HCl , then H_2S . Boil it, then add NH_4Cl , and NH_4OH . Finally add $(\text{NH}_4)_2\text{S}$. Filter the precipitate and try to dissolve it in dilute HCl . If it does not dissolve add *aqua regia*, then evaporate the free acid and add $\text{HC}_2\text{H}_3\text{O}_2$ and KNO_3 solution, leaving it for some hours.

MANGANESE.

436. The ores of manganese were formerly regarded as ores of iron. These were oxids, and were also called black magnesia. The metal has little use except in the manufacture of Bessemer steel. It is a multivalent element, the valences being 2, 3, 4, 6, 7. In the composition of its various oxids — MnO , Mn_2O_3 , Mn_3O_4 , MnO_2 , Mn_2O_7 — it resembles lead, and, in several compounds, chromium and iron.

437. History. — Scheele and Bergman, 1774, first showed that a metal different from iron was contained in MnO_2 . Gahn, about 1807, isolated the metal in a pure state.

438. Occurrence. — Its chief ore is *pyrolusite*, MnO_2 , and from this most of its compounds are made. Others are Braunitz, Mn_2O_3 , hausmannite, Mn_3O_4 , manganite, $\text{Mn}_2\text{O}_2(\text{OH})_2$, rhodochrosite, MnCO_3 . It is found in the Atlantic states from Maryland to Georgia. Deposits — to be worth exploitation — should have at least 60% of the oxid. Most American ore, as at present mined, is not fit for use in iron, as it contains some phosphorus. Spain and Germany have ores free from this element. Manganese compounds are quite widely distributed. Meteorites often contain uncombined Mn.

439. Reduction. — The ore is difficult to reduce, carbon being used for this purpose and a very high temperature employed.

440. Properties. — This is said to be the hardest of metals. It is brittle, almost infusible, and looks like cast iron. It easily oxidizes in the air, decomposes hot water, and dissolves in dilute acids. It forms alloys, and imparts valuable properties to steel, perhaps by combining with such impurities as sulfur and phosphorus, but this is uncertain.

Compounds. The *ous* compounds, *e.g.*, MnCl_2 , $\text{Mn}(\text{OH})_2$, are more stable than the *ic*, as $\text{Mn}(\text{OH})_3$ — contrary to the salts of iron or chromium. Manganous salts are pink. In manganates, as K_2MnO_4 , the valence of Mn is 6, and in permanganates, as KMnO_4 , it is 7. The latter salts are more stable and are used as oxidizing agents. MnO_2 is a black mineral, employed for the preparation of oxygen, of chlorine, and of the metal. A little added to molten glass

serves to correct the green color due to iron, and make the glass colorless. Added to pure glass it imparts an amethystine color.

441. Preparation. — To obtain oxygen MnO_2 is heated to a red heat, resulting in Mn_2O_3 and O . Write the equation and compute what proportion of the oxygen is thus obtained. Cl is obtained from HCl by its use. HNO_3 acts but slightly on MnO_2 but H_2SO_4 reacts with it liberating oxygen. $\text{H}_2\text{SO}_4 + \text{MnO}_2 = \text{MnSO}_4 + \text{H}_2\text{O} + \widetilde{\text{O}}$. What proportion of oxygen is liberated? A manganate is formed by heating MnO_2 — or other of the oxids — with an alkali and an oxidizing agent. $3\text{MnO}_2 + 6\text{KOH} + \text{KClO}_3 = 3\text{K}_2\text{MnO}_4 + \text{KCl} + 3\text{H}_2\text{O}$. CO_2 changes it into a permanganate. $3\text{K}_2\text{MnO}_4 + 2\widetilde{\text{CO}_2} = 2\text{K}_2\text{CO}_3 + \text{MnO}_2 + 2\text{KMnO}_4$. The two reactions show the manufacture of the most common permanganate, KMnO_4 . This salt is decolorized by SO_2 or by a ferrous salt. In fact iron is quantitatively analyzed by this means. NaMnO_4 is the basis of Condy's disinfecting fluid, which is useful in oxidizing putrescent organic matter. Manganates are green, permanganates purple. K_2MnO_4 is struc-

turally $\text{K}-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\parallel}}\text{Mn}-\text{O}-\text{K}$, and KMnO_4 is $\text{O}=\overset{\text{O}}{\underset{\text{O}}{\parallel}}\text{Mn}-\text{O}-\text{K}$.

442. Alloys. — *Spiegeleisen* and *ferromanganese* are alloys of Fe , Mn , and C . They are artificial products, the former containing 10 or 12% Mn , the latter 70 or 75. When the impurities have been mostly taken out of pig iron in the manufacture of steel, there is added a definite quantity of one of these substances. Its chemical function is not fully known, but Mn is supposed to unite with any oxygen, sulfur or phosphorus that may be left in the steel. At the same time it contains a definite, calculated quantity of combined carbon which unites with the iron and converts it into steel. Its main use in the steel manufacture is as a carrier of carbon.

443. Tests and Separations. — Alkalis precipitate from solutions of Mn^{++} salts $\text{Mn}(\text{OH})_2$, white if pure, but rapidly oxidizing to

$\text{Mn}_2\text{O}_2(\text{OH})_2$, brown. This precipitation is prevented by NH_4Cl solution. Mn is separated — with Co, Ni, and Zn — by precipitation as salmon-colored MnS by $(\text{NH}_4)_2\text{S}$. From CoS and NiS it is separated together with ZnS by its solubility in dilute HCl . From Zn it is separated by the solubility of salts of the latter in excess of strong NaOH solution, and the insolubility of $\text{Mn}(\text{OH})_2$.

Mn salts make the borax bead amethyst in the outer flame, colorless in the inner. Fused on platinum foil with Na_2CO_3 , they give green Na_2MnO_4 .

Exp. 249. — Heat a little MnO_2 to redness in an ignition tube, and thrust a glowing splint into the tube while it is heating.

Exp. 250. — To a solution of MnCl_2 add $(\text{NH}_4)_2\text{S}$. Filter and try to dissolve the residue in dilute HCl , then alkalize the solution with NaOH solution.

Exp. 251. — With a platinum wire make a borax bead and dip it into a solution of MnCl_2 , then fuse again. Try the same with a bead of Na_2CO_3 , and note the colors imparted.

Exp. 252. — Powder and heap up a little KMnO_4 . Make a hole in the heap and put in a few drops of glycerin. It is liable to inflame spontaneously.

Exp. 253. — Make a solution of KMnO_4 , 1g to 40^{cc} H_2O . Also make a similar solution of K_2MnO_4 . Keep for test solutions.

Exp. 254. — To some K_2MnO_4 solution add a few drops of dilute H_2SO_4 , then add H_2O . Boil some K_2MnO_4 solution and note the formation of $\text{Mn}_2\text{O}_2(\text{OH})_2$.

Exp. 255. — To some KMnO_4 solution add a few drops of H_2SO_3 . To a fresh solution add FeSO_4 solution.

Exp. 256. — Add 2 or 3^{cc} of dilute H_2SO_4 to 100^{cc} *stagnant* water — e.g., a hay infusion — then add 1 or 2 drops of KMnO_4 , and let it stand for an hour or two.

ZINC.

444. Zinc is one of the more important metals, and great quantities are annually produced. When amalgamated it constitutes the positive element of most galvanic batteries.

The so-called "galvanized iron" consists of sheets of iron or iron wire dipped into molten zinc, which forms a surface alloy and protects the iron from corrosion. Thus are combined the strength of iron and the durability of zinc. Thousands of tons of galvanized wire are yearly used for fences. Some of the alloys of zinc are brass (Cu, Zn), German silver (Cu, Zn, Ni), bronze (Cu, Sn, Zn).

445. History. — The date of the discovery of this metal is uncertain. Paracelsus mentions it about 1541, but probably it was known before, or at least its ores were previously used in the manufacture of brass.

446. Occurrence. — Zinc and lead present remarkable similarities in occurrence. The main ore of each is a sulfid, the two are usually associated, and both belong to the same geological formations. Sphalerite or blende, ZnS , Calamine, Zn_2SiO_4 , Smithsonite, ZnCO_3 , and zincite, ZnO , are common ores. Prussia, England, Belgium, and other European countries and the United States produce the metal.

447. Reduction. — The ore is first converted into ZnO by roasting. This is then reduced by heating with charcoal. As zinc boils at 940° , tubes or earthen mufflers are employed to condense the fine vapor which is called *zinc dust*, and to hold the liquid zinc. Heat liquefies the dust like sulfur flowers. It is then poured into moulds and is called spelter, containing impurities. Pure zinc is obtained by repeated distillation. Granulated zinc is made by pouring the molten metal into water. Of the three different sorts of apparatus for reducing the ore — the English, Belgian, and Silesian — the Belgian is shown in

Fig. 161. Inclined tubes of clay or iron about a meter long,

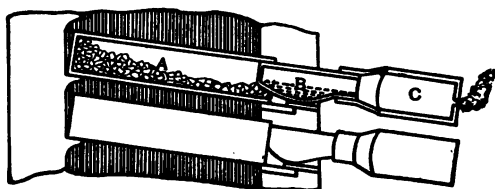


FIG. 161.

A, are placed in rows in a furnace. To the open end of each tube is adapted a short tube bulging downward, *B*,

to collect the zinc, and to the outer end of this is fitted an iron nozzle, *C*, having a small opening for gases to escape.

448. Properties. — This is a bluish white metal, not affected by dry air and very little by moist. Its properties vary with heat. It is quite brittle at the ordinary temperatures, but at 100° it can be rolled into sheets, while at 200° it is again brittle. It melts a little above 400°, and boils at not far from 1000°. Heated with air it fuses, then burns with a blue flame and throws off dense white fumes of ZnO, called flowers of zinc or philosopher's wool. In common acids it dissolves, liberating hydrogen from HCl or dilute H₂SO₄. If both acid and metal are pure scarcely any action occurs, especially with H₂SO₄, but a drop of PtCl₄ solution starts violent action between the two. Alkalis also dissolve zinc, forming zincates (*e.g.*, Na₂ZnO₂) and hydrogen.



449. Compounds. — The valence of zinc is two, hence it has but one class of salts. ZnO is made by burning the metal or by heating the nitrate, oxalate, carbonate, or hydroxid. Write equations for each process. It is used

somewhat as a constituent of white paint — called *zinc white*. Heating ZnO makes it temporarily yellow. ZnCl_2 has great affinity for H_2O , hence its use as a dehydrating agent and dryer of gases. It also has a caustic action and is used somewhat in surgery. It is an antiseptic and preserves from decay wood which has been soaked in it. It is employed in soldering metals, as it acts on the surface oxids and cleans the metals. ZnSO_4 can be made from Zn and H_2SO_4 , or by heating ZnS with access of air. It crystallizes with water, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Six molecules of H_2O are easily separated, but the seventh only at a high temperature. An old name for it was *white vitriol*. It is used in medicine and in cotton printing.

450. Tests and Separations. — Zinc is precipitated as ZnS — the only white sulfid — by $(\text{NH}_4)_2\text{S}$, together with Co , Ni , Mn , and Fe . H_2S does not precipitate it, because an acid is formed (with ZnCl_2 it is HCl) which dissolves the precipitate as fast as it is formed except from $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ or salts of weak acids. Acetic acid does not dissolve ZnS . Zn and Mn are separated from Co and Ni by the solubility of ZnS and MnS in dilute HCl . Zn is separated from Mn by the solubility of $\text{Zn}(\text{OH})_2$ — formed by NaOH — in excess of the NaOH solution (as Na_2ZnO_2) which must be pure, strong, and in excess, but not heated. $\text{Zn}(\text{OH})_2 + 2\text{NaOH} = \text{Na}_2\text{ZnO}_2 + 2\text{H}_2\text{O}$. $\text{Mn}(\text{OH})_2$ is not dissolved by NaOH .

When a zinc salt is heated, B.B.C.C., then moistened with $\text{Co}(\text{NO}_3)_2$ solution and reheated, it gives a greenish mass, CoZnO_2 , known as Rinman's green.

Zinc will precipitate most metals from solution, except Al , Cr , Mn , Ba , Sr , Ca , Mg , Na , K .

Exp. 257. — Heat a small piece of Zn in the oxidizing flame B.B.C.C. At a red heat it burns and coats the coal with ZnO , which is yellow when hot, white when cold. Put a drop of CoCl_2 solution on this incrustation and heat again.

Exp. 258. — Into a mixture of 1 part H_2SO_4 and 20 parts H_2O place a piece of zinc wire, then add 1 part of HgCl_2 solution and stir it with the wire. The zinc should become amalgamated.

Exp. 259. — Add $(\text{NH}_4)_2\text{S}$ to some ZnCl_2 solution, filter, try to dissolve the precipitate in dilute HCl , then add excess of NaOH solution. Acidify it with HCl and add $(\text{NH}_4)_2\text{S}$.

Exp. 260. — Make a mixture of these solutions: CoCl_2 , NiCl_2 , MnCl_2 , ZnCl_2 . Add dilute HCl , then H_2S , boil for some time and add NH_4Cl solution and NH_4OH (no precipitates should form with these), and finally $(\text{NH}_4)_2\text{S}$. This illustrates the separation of these metals from other groups in the course of analysis.

451. Uses. — Sheet zinc is used to line receptacles and reservoirs, to cover roofs of buildings and protect floors from heat. Batteries contain zinc amalgam. Alloys and galvanized iron have been described. Zinc dust is a reducing agent, and granulated zinc is also an essential in the chemical laboratory.

CHAPTER XXXVI.

IRON, ALUMINUM, CHROMIUM.

IRON.

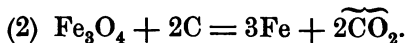
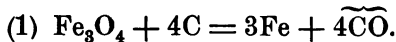
452. Of all metals iron is the most useful, and the one produced in largest quantity. The United States, Great Britain, Germany, and France are the greatest producers, each of these countries annually making millions of tons of pig iron and steel, which enter into innumerable products, from the locomotive to the watch-spring. As usually classed, iron is of three kinds, pig iron, steel, and wrought iron. *Pig iron* is the crude product of reduction of the ore, and contains much carbon, as well as many impurities. *Cast iron* is a variety of pig iron, and is used in castings, *e.g.*, stoves. *Steel* is a much purer, more compact, and harder form than these, is finely crystalline, and capable of being tempered so as to be made into pointed and cutting instruments, like knife and sword blades, needles, etc. Steel is also used for rails on railroads, and for other purposes where durability is desired. *Wrought iron* is not made in as large amounts as either of the others, is more tenacious, and less crystalline, and is very much the purest form. Piano strings are of very pure wrought iron, watch springs are of the finest steel. Nearly all the carbon in steel is chemically combined with the iron, while in pig iron much of it is dissemi-

nated through the mass, uncombined, in the form of visible particles of graphite.

453. History.—Iron is one of the seven original metals known to the ancients. Bessemer, in 1856, invented the present process of manufacturing steel, and thus revolutionized its use and production.

454. Occurrence.—Uncombined iron is found in one place on the coast of Greenland. Though the compounds of iron occur almost everywhere in the earth, only four ores have much value. These are *magnetite*, Fe_3O_4 , *hematite*, Fe_2O_3 , *limonite*, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and *siderite*, FeCO_3 . From the first two the iron made in this country largely comes, while siderite is the source of much of the foreign product. Magnetite is richest in iron, containing, when pure, over 72%, hematite having 70%, limonite some 60%, and siderite less than 50%. The ores often occur in bedded deposits in the oldest rocks, but sometimes in fissures. Pennsylvania is the great iron-smelting state.

455. Reduction.—The smelting of the ores to obtain pig iron consists in removing the oxygen from the compound by the reducing agency of carbon in some form, usually coke, obtained by the distillation of bituminous coal. Charcoal can be substituted where wood is abundant, as in Sweden, and anthracite has been used to a small extent. Both CO and CO_2 are formed.



The monoxid, CO , also becomes a reducing agent at the high temperature, as $\text{Fe}_3\text{O}_4 + 4\text{CO} = 3\text{Fe} + 4\widetilde{\text{CO}}_2$.

If the ore were pure, this would constitute the whole process, but there is always a large admixture of earthy matter called *gangue*, that contains infusible silicious compounds. This would seriously interfere with the reduction, if it were not made fusible. Lime, CaO , makes silica, SiO_2 , fusible, the reaction for which would be $\text{CaO} + \text{SiO}_2 = \text{CaSiO}_3$ (Chap. XXXII). No slag, however, has such a simple symbol. Carbonate of lime, CaCO_3 , is therefore added to the gangue, ore, and coke in the furnace. It is called a *flux*, because combined with the gangue it forms a liquid. Hence for the profitable reduction of iron there should be in near proximity, not only the ore, but also a deposit of limestone and of coal.

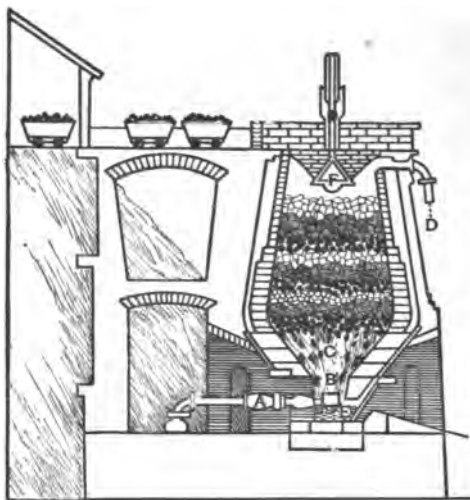


FIG. 162. — Blast furnace. *A*, tuyère; *B, C*, hottest part of furnace; *D*, tube for escape of gases; *E* (below tuyères), upper part slag, lower part molten iron; *F*, drop where fuel, ore, and flux are fed in.

The reduction is carried on in a blast furnace (Fig. 162), which may be 80 or 100 feet high and have a capacity of 12,000 cubic feet. It is constructed of brick and lined with silicious material. The fire once kindled is kept burning for months or years, or until the furnace needs repairing. The

fuel, flux, and ore are put in in alternate layers from the

top. A very high temperature is kept up by the burning of the coal, a blast of hot air being driven in at the bottom through pipes called *tuyères* (*tweers*). The intense heat and the carbon reduce the iron, which falls in drops to the bottom, whence it is drawn off into sand moulds, in bars called *pigs*. The limestone and gangue are also fused to a glass called *slag* that floats on the surface of the molten iron, and is thence drawn off. The upper and lighter part of the slag is very glassy, the part in contact with the iron is heavy, and contains considerable iron.

Pig iron contains many impurities, including the elements or compounds of C, Si, S, P, Mn. A very small fraction of one per cent of phosphorus will spoil an iron, and there must not be much sulfur, but pig iron always contains carbon.

From the top of the furnace such gases as N, H_2O , CO_2 , CO, etc., escape. These are used to heat the air which is forced through the *tuyères*.

456. Steel.—The manufacture of steel and of wrought iron consists essentially in removing most of the impurities — especially a large part of the carbon — from pig iron, but the processes for doing this are widely different in the two cases. The diverse properties of steel and wrought iron are due in part to the different processes as well as to the composition.

Bessemer steel is prepared

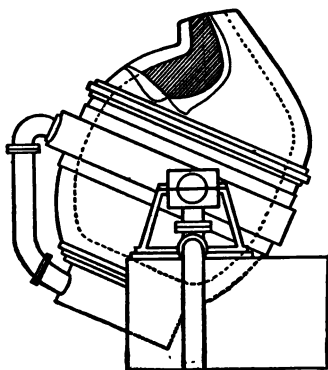


FIG. 163.

by melting pig iron, pouring it into a *converter* — a large iron “pitcher” holding five or ten tons, lined with silica, and hung on trunions (Fig. 163)—and blowing air through the molten mass. The oxygen unites with the C, S, etc., and forms the oxids, which escape as gases. If the air is forced in too long, the iron itself begins to oxidize, and the blast must be stopped at the exact moment, which is determined by an expert who watches the color of the flames as they issue. Some oxygen is left in the mass from the blast. To counteract this and to give other properties to the steel, *spiegeleisen* or *ferro-manganese* is added in definite quantity at this stage. Spiegeleisen is composed of some 10% Mn and 90% C, ferro-manganese of 70% Mn, 30% C. The exact cause of the effect which these have on the properties of steel is not known, but in part they furnish just enough carbon, and are supposed to counteract the bad effect of traces of S and P. The carbon is said to be “dissolved” by the steel, which is then run into moulds, as *ingots*. Ten tons of pig iron have been thus converted into steel in five minutes.

457. Wrought Iron.—In the manufacture of wrought

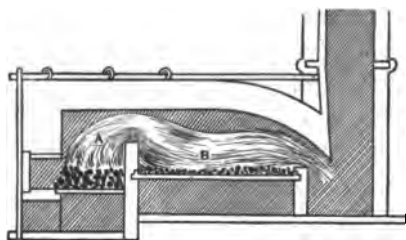


FIG. 164.

iron the impurities are burned out from pig iron in a reverberatory furnace. This has two connected compartments, one of which, *A*, contains the fuel, the other, *B*, the iron to be treated (Fig.

164). The coal is set on fire, and a strong draught causes

the heat, burning gases, and air to be reflected downward on the iron in the second compartment. The iron is intensely heated, being constantly stirred through holes in the side of the furnace — a process called *puddling* — and the product is iron having but a fractional per cent of carbon.

Steel may be made from wrought iron by carburizing the latter. Iron and charcoal are packed together and heated for some days, without melting, when it is found that in some unknown way solid carbon has penetrated solid iron. This is an expensive process, but the finer sorts of steel are made by it. Wrought iron can be made directly from iron ore in an open furnace with charcoal. This was the original mode.

	PER CENT (GENERAL).	PER CENT.	FUSIBILITY.
	Fe	C	
Pig iron	90	2-6	1200°
Steel	99	.5-2	1400°
Wrought iron	99.5	Fraction.	1500°

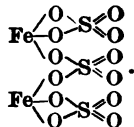
458. Properties. — *Pig iron* is coarsely crystalline, hence not ductile or malleable. It is hard and brittle, and cannot be welded. It is generally employed for castings. *Steel* is finely crystalline, and when suddenly cooled from red heat by plunging it into cold water, it becomes hard and brittle. The *temper* of the steel can afterwards be varied by heating to any required degree, which is indicated by the color of the oxid formed on the exterior, higher temperatures giving softer steel. *Wrought iron* is fibrous, as though composed of fine wires, and hence is malleable, ductile, tough, soft, and easily welded, but cannot be tempered.

All forms of iron oxidize in moist air, forming a scaly hydrated ferric oxid, *e.g.*, $\text{Fe}_2\text{O}_3 + \text{Fe}(\text{OH})_3$, but scarcely at all in dry air. Iron burns in oxygen with brilliant scintillations, forming Fe_3O_4 .

459. Salts.—Iron is either a dyad or a triad, and its salts are *ferrous* or *ferric*. The metal dissolves in the common acids with formation usually of ferrous salts, as FeCl_2 , FeSO_4 . These oxidize quite rapidly to ferric salts on exposure to air when in solution, $6\text{FeCl}_2 + 3\text{H}_2\text{O} + 3\text{O} = 4\text{FeCl}_3 + 2\text{Fe}(\text{OH})_3$, precipitating ferric hydroxid. Ferric salts are the more stable, and are yellow to reddish brown, whereas ferrous salts are greenish in color. Green clay owes its color to ferrous salts. When the clay is heated and made into bricks, the iron is oxidized to the ferric condition, and the bricks are red. The green color of grass and leaves is due to chlorophyll, which in turn is thought to get its color from ferrous salts. The red corpuscles of blood contain ferric iron. Oxidizing agents, as HNO_3 , change ferrous to ferric salts; reducing agents, as nascent hydrogen, ferric to ferrous.

Green vitriol, or copperas, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, is applied as a disinfectant, but its main use is for making black ink and dyes, by acting on nut galls. On exposure to air it effloresces, losing its water and becoming a white powder. It also oxidizes to $\text{Fe}_2(\text{SO}_4)_3$. FeS is the source of hydrogen sulfid, much used in analytical chemistry. FeS_2 , *pyrite*, is the source of much of the sulfur in sulfuric acid works. $\text{Fe}(\text{OH})_3$ is an antidote for arsenical poisoning, and other iron salts are used by physicians.

Structurally FeSO_4 is: $\text{Fe} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{S} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array}$. $\text{Fe}_2(\text{SO}_4)_3$ is:



460. Tests and Separations.—Salts of Fe'' and Fe''' B.B.C.C. give in the outer flame a yellow bead, yellowish red when hot, in the inner a bottle green. Fe'' salts give with soluble hydrates a dirty green precipitate of $\text{Fe}(\text{OH})_2$. Fe''' salts give a red-brown precipitate of $\text{Fe}(\text{OH})_3$. With potassium ferrocyanid, K_4FeCy_6 , salts of Fe'' give a bluish white precipitate, Fe''' a deep blue. With potassium ferricyanid, K_3FeCy_6 , salts of Fe'' give a dark blue precipitate, Fe''' a green or brown color only. With potassium sulfocyanid, KSCy , salts of Fe'' do not react, but Fe''' salts give a blood-red color, but no precipitate. In analysis Fe'' salts should be oxidized to Fe''' with HNO_3 . Fe is separated from Al in solution by the solubility of the latter salts in excess of NaOH solution.

Exp. 261.—Dissolve some iron filings in HCl in an open test tube or receiver. When action stops, filter, and save the filtrate for other tests.

Exp. 262.—Take part of the above solution, add a *very* few drops of aqua regia, and then heat it. Fe'' should oxidize to Fe''' .

Exp. 263.—Distinguish Fe'' from Fe''' salts by pouring some FeCl_2 solution (from Exp. 261) into four test tubes, and into four others some FeCl_3 solution (from Exp. 262). Now to one tube of each class add NaOH solution, to another of each K_4FeCy_6 solution, to a third K_2FeCy_6 solution, and to the fourth KSCy solution (a drop or two). Compare the results.

Exp. 264.—Dissolve Fe in dilute H_2SO_4 , filter, and try to oxidize the filtrate to Fe''' with HNO_3 —a drop at a time— heating it meantime.

Exp. 265.—Try to reduce Fe''' to Fe'' , by putting a piece of zinc into a test tube containing a solution of FeCl_3 , and then adding a few drops of HCl . When action stops, test the solution with NH_4OH .

Exp. 266.—Add solutions of each of these in succession to a solution of FeCl_3 , and note the result: HCl , H_2S , NH_4OH , $(\text{NH}_4)_2\text{S}$.

Exp. 267.—Into a borax bead fuse a little FeSO_4 solution in the reducing flame. Observe the color when hot, and when cold. Make another bead, and fuse the solution in the oxidizing flame. Again try FeCl_3 solution in each flame.

Exp. 268.—Powder a small ferrous sulfate crystal, and heat in an ignition tube. It melts in the water of crystallization, and if heated enough, will break up into Fe_2O_3 , SO_2 , and SO_3 . Put away for a few days a small crystal of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ on a piece of paper.

ALUMINUM.

461. Aluminum has so many of the useful properties of metals and so few defects that when it can be obtained in large quantity at a low price, it may take the place of iron, tin, copper, and other metals for many purposes, as it combines lightness, strength, and non-corrosibility. Formerly, when it took three pounds of sodium to separate one pound of aluminum, the cost was \$15 or more per pound. Now (1897) the cost is 40 to 50 cents a pound.

462. History. — Wöhler, 1827, first separated the metal by the reducing action of Na. Subsequently it was obtained by electrolysis, and, in 1885, by the reducing action of carbon, the high temperatures of the electric furnace being made use of. The highest temperature of combustion — the oxy-hydrogen flame — is some 2000° or 2200° , which was insufficient to effect reduction of Al, but since the application of the dynamo, temperatures of 3500° or 4000° are obtained by the electric furnace, high enough in fact so that every oxid — except those of C — can be reduced by carbon. Hall, 1886, invented the method now in use of obtaining it from igneous solution by the use of a flux.

463. Occurrence. — In its compounds, which are mostly silicates, aluminum is very abundant and the most widely distributed of metals, but it never occurs uncombined. Clay, feldspar, mica, slate, etc., are silicates of it. It is found in all rock formations except limestone, and in nearly two hundred minerals. Though occurring in all soils, it is not taken up by plants, except by a few cryptogams. *Corundum*, Al_2O_3 , is the richest of its ores, and emery is a mixture of the oxids of Al and Fe. Compounds of Al are very difficult of reduction. *Bauxite*, a hydrous oxid of Al found in France, and cryolite, Na_3AlF_6 , occurring in Greenland, are sources of the metal and its compounds. The ruby and sapphire are Al_2O_3 colored by impurities.

464. Reduction. — Aluminum is now reduced from prepared Al_2O_3 by an electrical process invented by Hall. Large wrought-iron tanks (Fig. 165) are lined with carbon, *B*, which forms the negative electrode, or cathode. The positive electrode, or anode, *A*, consists of large carbon terminals. The current is passed over large copper wires attached to anode (+) and cathode (—). Into the carbon-lined tank is put a flux, *C*, consisting of a mixture of artificial cryolite and of fluorite, which will

dissolve some 25% of Al_2O_3 . When the current is turned on, the flux is melted by the heat generated by its resistance. The flux melts and dissolves the Al_2O_3 that is fed in from time to time. At *C* the Al_2O_3 is electrolyzed by the current, the oxygen going to the carbon anode and combining with it to form CO , the liquid aluminum going to the cathode at the bottom, *D*, whence at intervals it is ladled out. $\text{Al}_2\text{O}_3 = 2\text{Al} + 3\text{O}$. $\text{C} + \text{O} = \text{CO}$. By this process a purity of 97% Al can be obtained. Subsequently it is purified to 99%.

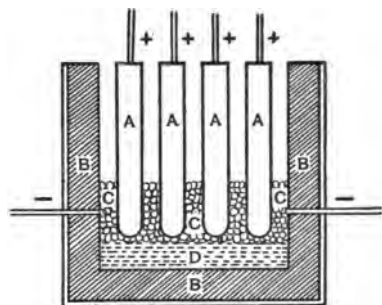


FIG. 165.

465. Properties. — This is a silvery white metal, lighter than glass, and only one-third the weight of iron. It can be easily cut, hammered, and cast, but not readily welded — except by electrical welding. It alloys with most metals, forming with them many valuable compounds. In malleability it ranks next to Au and Ag, but is not very ductile. It is a good conductor of electricity. The metal melts at 650° , but shrinks $2\frac{1}{4}\%$ on solidification.

Aluminum does not oxidize in dry air, and not much in moist, nor do H_2S , CO_2 , etc., corrode it. Nitric acid does not affect it, and H_2SO_4 very slowly dissolves it. It readily dissolves in HCl , giving rise to AlCl_3 and H . It is also dissolved by fixed alkalis. $2\text{NaOH} + 2\text{H}_2\text{O} + \text{Al} = \text{Na}_2\text{Al}_2\text{O}_4 + 6\text{H}$.

466. Compounds.—The element is a triad. Most of its compounds can be made from the sulfate $\text{Al}_2(\text{SO}_4)_3$, and this from the silicate as it exists in alum shale, which, besides the silicate of aluminum, contains some FeS_2 . The broken shale is piled into heaps with coal, and is set on fire and partially covered so as to smoulder. Part of the sulfur of the FeS_2 becomes SO_2 , which with oxygen and water forms H_2SO_4 , and unites with the aluminum compound to make $\text{Al}_2(\text{SO}_4)_3$. The FeS_2 is reduced to FeS , then oxidized by the air to FeSO_4 . The process is a slow one, and water is added from time to time for some months. The soluble substances $\text{Al}_2(\text{SO}_4)_3$ and FeSO_4 are then dissolved in water and concentrated. FeSO_4 first crystallizes out, and can be changed to K_2SO_4 by KCl . A mixture of $(\text{Al}_2\text{SO}_4)_3$ and K_2SO_4 in the ratio of their molecular weights forms *alum*, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, on evaporation.

467. Alums.—An alum is a double sulfate, usually of aluminum, or chromium or ferric iron, and one of the alkali metals. Though about one hundred alums are theoretically possible, the two most common are those of NH_4 and K . From the sulfate of aluminum can be made the insoluble compounds by precipitation, and from the hydroxid (which is insoluble) the soluble ones, by solution in acids.

468. Mordants.—In cloth that is to be printed, like calico, or even dyed, the pigment often requires something to fasten it to the fiber in order to make it a *fast* color so that it will not wash out. A substance which will do this is a *mordant*—a word meaning “to bite,” since the substance bites into the fiber of the cloth and at the same time takes hold of the coloring material and “precipitates” it on the cloth. Cotton cloth especially requires mordants more than woolen or silk goods. Certain salts of Al , *e.g.*, the acetate, are much used for mordants. The cloth is first dipped into a solution of mordant, then after drying, the coloring matter is applied.

469. Tests.—(1) Heated B.B.C.C. salts of Al reduce to white Al_2O_3 , which on reheating with a drop of CoCl_2 solution becomes blue. (2) $(\text{NH}_4)_2\text{S}$ or NH_4OH precipitates white gelatinous $\text{Al}(\text{OH})_3$. Al_2S_3 does not form in solutions. $3(\text{NH}_4)_2\text{S} + 2\text{AlCl}_3 + 6\text{H}_2\text{O} = 2\text{Al}(\text{OH})_3 + 6\text{NH}_4\text{Cl} + \overbrace{3\text{H}_2\text{S}}^{\text{precipitate}}$. (3) NaOH will first precipitate $\text{Al}(\text{OH})_3$ from solutions, but excess of NaOH dissolves the precipitate to sodium aluminate, $\text{Na}_2\text{Al}_2\text{O}_4$. $2\text{Al}(\text{OH})_3 + 2\text{NaOH} = \text{Na}_2\text{Al}_2\text{O}_4 + 4\text{H}_2\text{O}$. This is like the action on zinc salts, but NH_4Cl reprecipitates $\text{Al}(\text{OH})_3$, but not zinc hydrate; whereas H_2S reprecipitates the zinc salt, but not the Al . (4) This

solubility in excess of NaOH distinguishes Al from Fe''' and Cr''' salts. (5) The iron group of metals, Fe, Cr, Al, is separated from the silver group by the inaction of HCl on the former, and from the copper and tin groups by the inaction of H_2S .

470. Uses.—The metal finds employment in many household utensils and small wares, thimbles, horseshoes, surgical instruments, flying-machines, etc. It is mainly applied in alloys of copper and steel. Aluminum bronze, 90% Cu and 10% Al, resembles gold in color and lustre. The bulk of Al is used in steel alloys. Its production and use have greatly increased in the last two or three years.

Exp. 269.—Put a drop of HCl on a piece of Al, and look for effervescence; or add HCl to a piece of Al in a test tube. Try also HNO_3 and H_2SO_4 , strong and dilute.

Exp. 270.—To a solution of AlCl_3 add a little NaOH solution. If a precipitate falls, add excess. If it clears, add NH_4Cl solution to a portion and H_2S to another part. Separate Zn and Al from solutions of their chlorids. Separate Fe and Al from FeCl_3 and AlCl_3 .

Exp. 271.—Add $(\text{NH}_4)_2\text{S}$ to some AlCl_3 solution. Also add NH_4OH to another portion. To a third add H_2S .

Exp. 272.—Heat strongly a small piece of $\text{Al}_2(\text{SO}_4)_3$ B.B.C.C. Put a drop of CoCl_2 solution on the residue, and heat again.

Exp. 273.—Mix solutions of FeCl_3 , AlCl_3 , CrCl_3 in a test tube, and add dilute HCl, then H_2S , finally NH_4Cl and NH_4OH .

Exp. 274.—Dip a piece of white cotton cloth into a strong solution of indigo or cochineal. After a minute wring it out and dry it. Dip another piece into a solution of aluminum acetate and dry it, then dip it into the solution of indigo or cochineal and dry it again. When they are dry, try to wash the color from both pieces.

CHROMIUM.

471. The word *chromium* is derived from the Greek, and means *color*. Its compounds are almost all colored.

and furnish many brilliant pigments — red, yellow, green, etc. The element is of no account, but its salts — chromous, chromic, chromate, and dichromate — are of much importance. It acts as a metal in some cases, as a non-metal in others, forming chromic acid, and also the base chromic hydrate. Its presence in minute quantity colors minerals, as emerald, olivine, and serpentine.

472. History. — Chromium was discovered, in 1797, by Vauquelin in crocoite.

473. Occurrence. — The main compound is *chrome iron* or *chromite*, FeCr_2O_4 . It also occurs as crocoite, PbCrO_4 , but is never uncombined, and its compounds are not widely diffused nor abundant.

474. Reduction. — The metal can be obtained by electrolyzing the chlorid, CrCl_3 , or by reducing it with sodium. The chief compound of commerce is *potassium dichromate*, $\text{K}_2\text{Cr}_2\text{O}_7$, a stable, red, crystalline, soluble solid. It is obtained by fusing a mixture of FeCr_2O_4 , $\text{Ca}(\text{OH})_2$, and KOH , which results in Fe_2O_3 , CaCrO_4 , and K_2CrO_4 . The last two are dissolved in water, and changed to the dichromate by addition of any dilute acid, when $\text{K}_2\text{Cr}_2\text{O}_7$ will crystallize out.

475. Properties. — A whitish gray metal, very hard, infusible except in the oxy-hydrogen flame, it burns only at a very high temperature to Cr_2O_3 . The metal alloyed with steel imparts a special hardness to the latter.

476. Compounds. — Cr has three valences, viz., 2, 3, and 6, as in CrO , Cr_2O_3 , CrO_3 , called chromous oxid, chromic oxid, and chromic anhydrid (also called chromic acid, $\text{CrO}_3 + \text{H}_2\text{O} = \text{H}_2\text{CrO}_4$). The chromous salts are unstable and of small importance. The chromic and chromate salts are often met with. The former are obtained from the latter by reducing agents, such as H_2S , SO_2 , or HCl with a little alcohol. Chromates are obtained from chromic salts by oxidizing agents, as KClO_3 , Cl , etc. Chromates are usually yellow in color, dichromates (confined mostly to alkali metals) are red, whereas chromic salts are usually green, but sometimes violet. Acids change the alkali chromates to dichromates (also called acid chromates), alkalis change dichromates to chromates. In CrO_3 , K_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, etc., the valence of Cr is 6. Insoluble chro-

mates are made equally well with either chromate or dichromate, *e.g.*, $\text{BaCl}_2 + \text{K}_2\text{CrO}_4 = \text{BaCrO}_4 + 2\text{KCl}$, or $2\text{BaCl}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} = 2\text{BaCrO}_4 + 2\text{KCl} + 2\text{HCl}$. The one salt differs from the other as follows : $\text{K}_2\text{CrO}_4 + \text{CrO}_3 = \text{K}_2\text{Cr}_2\text{O}_7$.

Chrome yellow is PbCrO_4 , chrome red Pb_2CrO_5 , chrome orange a mixture of the two, chrome green $\text{H}_4\text{Cr}_2\text{O}_5$, and chrome alum is $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

Exp. 275. — To a solution of K_2CrO_4 add dilute HCl , and shake it well. To a solution of $\text{K}_2\text{Cr}_2\text{O}_7$ add a little NH_4OH .

Exp. 276. — Add HCl and a little alcohol to a solution of $\text{K}_2\text{Cr}_2\text{O}_7$ in a test tube, and boil, noting the change in color. Try H_2S with $\text{K}_2\text{Cr}_2\text{O}_7$ solution.

Exp. 277. — Boil in an evaporating dish CrCl_3 solution nearly to dryness, then add a crystal of KClO_3 , and boil to dryness. Add a cubic centimeter of water, and if it is still green, boil again, and add another crystal of KClO_3 . Repeat till a red color is obtained.

Exp. 278. — Add BaCl_2 solution or $\text{Pb}(\text{NO}_3)_2$ solution to separate solutions of K_2CrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$.

Exp. 279. — Into one test tube pour $\text{K}_2\text{Cr}_2\text{O}_7$ solution, into another CrCl_3 solution. To each add NH_4Cl solution and NH_4OH . The result distinguishes Cr''' and Cr^{I} .

477. Tests and Separations. — (1) Chromium compounds color the borax bead emerald green. (2) An insoluble salt should be fused with a mixture of KNO_3 and Na_2CO_3 , which oxidizes chromium to a chromate. This is dissolved, acidified with $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ added, when PbCrO_4 is precipitated, as yellow powder. (3) A chromate or dichromate is tested for by adding AgNO_3 solution. The precipitate is reddish brown Ag_2CrO_4 . (4) BaCl_2 solution gives yellow BaCrO_4 . (5) H_2S reduces the red or yellow *ate* salt to green *ic*. (6) Hydrogen dioxid, H_2O_2 , imparts a blue color (HCrO_4) to a solution acidified by H_2SO_4 . This is best shown by adding ether.

Exp. 280. — Fuse into a borax bead a little CrCl_3 solution, first in the outer, then in the inner flame, and note the colors when hot, and when cold. Try the same with $\text{K}_2\text{Cr}_2\text{O}_7$ solution.

Exp. 281. — To some K_2CrO_4 or $K_2Cr_2O_7$ solution add $AgNO_3$ solution.

Exp. 282. — To K_2CrO_4 solution add a very little dilute H_2SO_4 , then dilute H_2O_2 solution and a little ether.

478. Uses. — The metal is used to harden steel. The salts are used as coloring materials in dyeing wool, in printing calico, and in paints.

CHAPTER XXXVII.

ARSENIC, ANTIMONY, TIN.

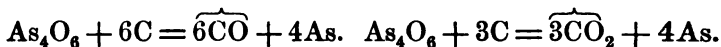
ARSENIC.

479. While one of the compounds of arsenic is a common poison, there is no drug that is easier or more certain of detection, for by Marsh's test a ten-millionth (according to some experimenters a two-hundred-millionth) part of arsenic in a solution has been detected. Bodies have been exhumed twenty years after burial and the unerring evidence of poisoning found. The compounds of this element give a variety of brilliant colors, and were formerly used, as to some extent they are now, for pigments, especially green and yellow.

480. History. — The alchemists were acquainted with the ores of arsenic. Geber knew the oxid and Albertus Magnus speaks of the metal, but in 1773 Brandt first showed that white arsenic is obtained by burning the metal. The oxid was used in medicine by Paracelsus in the sixteenth century for skin diseases.

481. Occurrence. — The metal is found native in small quantities only, notably in Germany. The main ore from which the element and its chief commercial compound are obtained is *arsenopyrite*, FeAsS . This is quite widely distributed, but the products come mainly from Germany and England. *Realgar*, As_2S_3 , which is red, and *orpiment*, As_2S_3 , yellow, are other ores; it is also obtained as a by-product in reducing ores of Ni, Co, etc., with which it forms arsenids, as CoAs_2 .

482. Reduction. — Arsenical pyrites, FeAsS , are oxidized by roasting them, *i.e.*, heating with access of air. This gives oxids of the three elements, Fe_2O_3 , As_4O_6 , SO_2 . The first remains behind in the retort, the others are gaseous, but As_4O_6 soon sublimes, while SO_2 escapes as a gas. As_4O_6 is purified by resubliming. Metallic arsenic is obtained by reducing the oxid with charcoal.



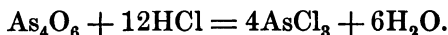
Exp. 283. — Mix enough As_4O_6 to cover the blade of a small penknife with an equal bulk of fine charcoal, drop the mixture into a small, dry ignition tube, and heat it strongly.

Exp. 284. — Powder a little FeAsS , put it into an ignition tube, and heat strongly. Observe any vapor or sublimate and note any odor.

483. Properties. — *Physical.* Arsenic has certain properties which ally it with metals, and others that are non-metallic. It is a grayish white, crystalline substance of metallic lustre, easily volatile, poisonous, having, when vaporized, the odor of garlic. When alloyed with lead it hardens the latter, for which reason it is used in shot manufacture. When roasted it combines with oxygen, forming arsenious oxid, As_4O_6 . Its combustion may be shown by putting some into a piece of ignition tubing and passing a current of oxygen over it, while a Bunsen flame is placed directly underneath the arsenic. It burns with a blue flame. In a current of hydrogen under similar conditions it volatilizes and sublimes. It has great attraction for chlorin, and when sifted into the dry gas often burns spontaneously with scintillations, like Sb, giving AsCl_3 . $\text{As} + \widehat{3\text{Cl}} = \text{AsCl}_3$.

Exp. 285. — Sprinkle a pinch of powdered metallic arsenic into a receiver of dry chlorine gas.

484. Oxids. — Two oxids are known, arsenious, As_4O_6 (often written As_2O_3), and arsenic, As_2O_5 . The former only is important. It is the most abundant commercial compound of the element and is often called *white arsenic* or simply *arsenic*. From this, other compounds of the metal are formed. Its method of preparation has been indicated. It is a white substance, sometimes amorphous, sometimes crystalline, which when pulverized resembles flour, but is heavier and has a sweetish taste. It dissolves very slightly in water, on which its particles seem to have a repellant action. On boiling for a long time more dissolves. Hydrochloric acid and alkalis are the best solvents. With HCl it forms AsCl_3 .



From this solution the insoluble salts, like As_2S_3 and Scheele's green, are easily made.

485. Physiological Effects. — Like other arsenical compounds, the oxid is very poisonous, the lethal dose being about $2\frac{1}{2}$ grains or $\frac{1}{8}$ gram. It is called an *irritant* poison, and acts rather slowly, as the digestive fluids have first to transform it before absorption. The antidote is ferric hydrate, $\text{Fe}(\text{OH})_3$, freshly prepared, together with magnesia. This forms a compound of arsenic insoluble in the fluids of the body. An overdose may act as an emetic. Very small doses of arsenic seem to act as a tonic. Its habitual use in small doses imparts a plumpness to the form and softness to the skin, improves the breathing, and aids the secretion of fat. For these reasons it is fed to worn-out horses and to asthmatic persons. The mountaineers of southern Austria are addicted to its use, and mountain climbing is said to be less fatiguing because of the greater ease in breathing when the system contains arsenic. Like other poisons, its use is to be deprecated. The devotee of the poison, on attempting to leave it off, has all the symptoms of arsenical

poisoning. Workmen in the reduction of arsenic have their mouths and noses covered with moist cloths and their bodies encased in leather. All compounds of arsenic are poisonous.

486. Salts.—There are two classes of salts, the *ate* and the *ite*, of which sodium arseniate, Na_3AsO_4 , and sodium arsenite, Na_3AsO_3 , are examples. In the former case the valence of As is 5, in the latter 3. The *ite* salts are more commonly met with. The sulfid, As_2S_3 , is a permanent and brilliant yellow pigment made by passing H_2S gas into a solution of an *ite* salt. Scheele's green, HCuAsO_3 , and Schweinfurt or emerald green, $\text{Cu}(\text{AsO}_2)_2 \cdot \text{CuAsO}_2 \cdot \text{C}_2\text{H}_5\text{O}_2$, both go under the name of *Paris green*, and are much used as pigments, especially for green window blinds, shipping tags, silks, etc. Wall papers at one time almost always contained arsenic, but now—owing to better substitutes and to legislative prohibition—they rarely have it. Scheele's green is made by adding a solution of some copper salt, as CuCl_2 , to an arsenious salt solution, as HNa_2AsO_3 . If these are nearly neutral a precipitate of HCuAsO_3 is obtained, but if strongly acidified with HCl or alkalinized with NH_4OH , no precipitate falls, which is the same as saying that Scheele's green is soluble in either of the reagents.

Exp. 286.—To a nearly neutral solution of HNa_2AsO_3 add CuCl_2 solution. Divide the product, after shaking it, into two parts. To one add HCl , to the other NH_4OH .

487. Tests.—Four of these are important—Marsh's, Reinsch's, the carbon, and the hydrogen sulfid tests.

(1) *Marsh's* is the most delicate and interesting, and consists in first forming arsin, AsH_3 , then decomposing it and subliming the arsenic. Any soluble arsenical compound in presence of nascent hydrogen forms arsin, which is readily decomposed by heat, when the arsenic sublimes. By this process a quantity far too small for the most delicate balance can be detected, in fact a mere trace of the element. Suppose we wish to ascertain whether a common green shipping tag contains arsenic (1 or 2^{cem} will be enough), proceed as below.

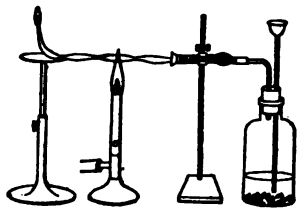


FIG. 166.

Exp. 287.—Prepare a hydrogen generator with drying attachment and a tube of hard glass, constricted at one or two places and ending in a lamp tube (Fig. 166). Have all the chem-

icals perfectly pure, using C. P. zinc and HCl, also distilled water, so that no As can come from them. After testing the escaping gas and lighting it, pour through the thistle tube a solution of the substance supposed to contain As, — e.g., one obtained from 1 or 2^{gm} of a green tag put into HCl, which would form AsCl_3 and dissolve it. If As is present, the flame becomes whiter in color and a porcelain dish held in it condenses metallic arsenic as a black metallic spot. A Bunsen flame under the hard glass tube decomposes the AsH_3 and sublimes the As in the capillary beyond, where it condenses as a black metallic mirror. Dip the tube into NaClO solution.

Explanations.—Suppose the pigment to have the composition AsX_3 , in which X is any non-metallic monad. HCl gives this reaction: $\text{AsX}_3 + 3\text{HCl} = \text{AsCl}_3 + 3\text{HX}$. Nascent hydrogen decomposes AsCl_3 and combines with both elements. $\text{AsCl}_3 + 6\text{H} = \text{AsH}_3 + 3\text{HCl}$. The arsin passes out and is burned together with the excess of hydrogen. $4\text{AsH}_3 + 12\text{O} = \text{As}_4\text{O}_6 + 6\text{H}_2\text{O}$. The interposition of porcelain cools the flame below the kindling-point of arsenic (which sublimes), so that only hydrogen then burns. $2\text{AsH}_3 + 3\text{O} = 2\text{As} + 3\text{H}_2\text{O}$. A Bunsen flame decomposes the arsin: $\text{AsH}_3 = \text{As} + 3\text{H}$, when the metal sublimes in the capillary tube. The question arises whether any other element than arsenic would act in a similar way. Antimony acts almost exactly like it, forming gaseous and combustible stibin, SbH_3 , which likewise decomposes and sublimes as a metallic mirror. Several tests serve to distinguish the sublimed As from Sb, the best of which is the solubility of As in sodium hypochlorite, NaClO, and the insolubility of Sb. The quantity of As can be determined by comparing the depth of shading of the deposit with that of tubes containing a known quantity.

(2) *Reinsch's Test.* This consists in depositing As on copper, then oxidizing the As and subliming the As_4O_6 formed.

Exp. 288.—Dissolve the arsenic from the substance, as before, in HCl, then put into the evaporating dish or test tube containing it a small and thin, but bright strip of Cu foil, and heat the mixture for a moment. The As deposits on the Cu and blackens it. Finally remove the Cu, dry it between blotting-papers, cut it into narrow strips, and put these into a small dry tube. Heat the tube and note any sublimate.

Explanation.—The compound of arsenic was first changed to AsCl_3 by HCl. Copper in the heated acid withdrew the arsenic and deposited it, leaving CuCl_2 in solution. Heat vaporized the arsenic,

which at the same time combined with the oxygen in the tube to form As_4O_6 , and this in turn sublimed as a white solid on the cold sides of the tube. To identify the compound it must be examined under a microscope, when a portion of it will contain crystals like those in Fig. 167. Some of the sublimate is amorphous. Write all the equations for the action outlined above.



FIG. 167.

test. This was described in a previous experiment.

(4) *Hydrogen sulfid* precipitates arsenious sulfid, As_2S_3 (yellow), from an acid solution of any arsenious salt, *e.g.*, $AsCl_3$. $2AsCl_3 + \overbrace{3H_2S} = As_2S_3 + \overbrace{6HCl}$. Cadmium sulfid, CdS , formed in the same way, is also yellow, but may be distinguished by being insoluble in ammonium polysulfid, $(NH_4)_2S_x$, whereas As_2S_3 is soluble.

Exp. 289. — To a solution of HNa_2AsO_3 in water and HCl add H_2S in solution, or as a gas. Filter and wash the precipitate, and try to dissolve it in $(NH_4)_2S_x$.

Exp. 290. — Try the same experiment with $CdCl_2$ solution and compare results. Arsenic is separated from tin and antimony by the insolubility of its sulfid, As_2S_3 , in HCl . SnS and Sb_2S_3 are soluble in it. Also by the solubility of As_2S_3 in $(NH_4)_2CO_3$ solution.

Exp. 291. — Mix solutions of $AsCl_3$, $SbCl_3$, $SnCl_2$ (in HCl and H_2O), and precipitate the sulfids with H_2S . Filter the product and divide the residue into two parts. To one add HCl , warm it for some time, and filter. Test the *filtrate* by Marsh's test, and try to dissolve the sublimate in $NaClO$. Dissolve the *residue* in $(NH_4)_2CO_3$, and add HCl and H_2S . To the other part add $(NH_4)_2CO_3$ solution, filter and test the *filtrate* as before.

Arsenical Poisoning. — For evidence of arsenical poisoning in post-mortem examination of the liver, the stomach, etc., these organs and their contents are sometimes dialyzed before the Marsh and other

tests can be applied, in order to separate the arsenic from the viscera and food products. After being treated with HCl , KClO_3 , etc., the finely divided substances are put into the dialyzer (Fig. 168) and suspended over water, when the arsenic compounds, being more diffusive, pass through the membrane into the water of the outer vessel, leaving the other substances behind. This outer solution is then concentrated and tested for arsenic. Generally, however, the contents with the arsenic are dissolved in aqua regia and then tested by Marsh's or Reinsch's test.

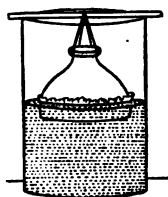


FIG. 168.

488. Uses.—Metallic arsenic has few uses. It is employed in shot manufacture, being alloyed with the molten lead in order to harden the latter. It is used to some extent in fly and rat poisons. The oxid, As_4O_6 , is applied in medicine, in poisons, by manufacturers of anilin colors, by dentists to kill the nerves of teeth, by taxidermists as a preservative of skins, and by horse-jockeys and arsenic-eaters, also as the basis of other arsenical compounds. Paris green is used to destroy the potato beetle, the gypsy moth, etc., and enters into many green paints. Fowler's solution, an arsenite of potassium, is employed in medicine as an antidote for malarial diseases.

ANTIMONY.

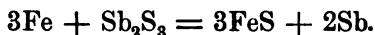
489. Although antimony has a very brilliant metallic lustre, some of its properties, especially its acid-forming ones, place it with the non-metals. In valence and in compounds both this element and bismuth naturally fall into the same group with nitrogen, phosphorus, and arsenic.

490. History.—No element used in medicine has a more interesting history than antimony since Basil Valentine wrote his "Triumphal

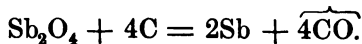
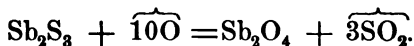
Car of Antimony," in which he refers to it as the "great stone of the ancient philosophers." So thoroughly did he study the element and its compounds in the fifteenth century, that but little was added to the knowledge of them till the nineteenth century. He experimented with them in many ways. He is said to have fed some lean swine with a compound of it. Finding it agreed with them, he next tried it on some monks, whom it killed. For this reason he is said to have named it antimony (anti-monk). The story, while probably not true, illustrates the zeal of Valentine in using chemicals as medicine. The element appears to have been known long before Valentine's day, but it was very long confounded with bismuth. Valentine mentions it as used in printers' type and in bells. For a hundred years, from 1566 to 1666, the use of antimony in medicine was prohibited in Paris.

491. Occurrence.—The chief compound from which antimony is obtained is *stibnite*, Sb_2S_3 (whence the Latin name of the element, *stibium*). This mineral is abundant in some places, *e.g.*, in Japan, where it occurs in very large crystals. Many other sulfids contain antimony, and it is found uncombined in small quantities, but is not widely diffused.

492. Reduction.—There are two methods of reduction from the sulfid. (1) Scrap iron is mixed with it and heated in crucibles. The iron combines with the sulfur, the antimony sinks to the bottom, and the ferrous sulfid remains on top.



(2) Stibnite is oxidized to antimony tetroxid, Sb_2O_4 , by roasting, and the oxid is then reduced with carbon and heat.



Exp. 292. — Cautiously mix a little powdered stibnite with its bulk of potassium cyanid (which is a deadly poison), put the mixture on charcoal, and blow the flame against it (Fig. 169). Notice the metallic globule and the fumes which rise. When cool try to crush the residue, and to dissolve it in *aqua regia*.

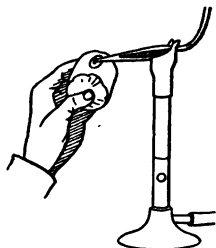


FIG. 169.

493. Properties. — This is a silvery white solid of brilliant metallic lustre; it does not tarnish at usual temperatures. Antimony is brittle and breaks in layers. It melts at 450° , and expands slightly in solidifying, thus filling every line, for which reason it is valuable as a constituent of material for casts and type-metal. It is not a very good conductor of heat or electricity, but burns at a red heat, giving dense fumes of the trioxid and tetroxid, Sb_2O_3 , Sb_2O_4 . Antimony will scarcely dissolve in hydrochloric acid unless a few drops of nitric are added to form *aqua regia*, in which it dissolves readily to SbCl_3 . It is not soluble in HNO_3 , but reacts with it to form H_3SbO_4 or Sb_2O_3 . H_2SO_4 forms $\text{Sb}_2(\text{SO}_4)_3$. The element as well as its oxid sometimes plays the part of a base, as in the chlorid or sulfate, at others that of an acid, as in antimonious acid, H_3SbO_4 , or orthoantimonious, H_3SbO_3 . Antimony itself is not regarded as a poison, but its soluble compounds are all poisonous. It combines vigorously with Cl, Br, and I.

494. Compounds. — This element is usually trivalent, sometimes quinquivalent, its oxids being Sb_2O_3 and Sb_2O_5 , also Sb_2O_4 . Its salts are not of special importance, the chlorid, SbCl_3 , and oxychlorid, SbOCl , the sulfid, Sb_2S_3 , the hydrid, SbH_3 , and tartar emetic, $\text{KSbOC}_4\text{H}_4\text{O}_6$, being most useful. The oxychlorid, or basic chlorid, SbOCl , is formed by the reaction of SbCl_3 (butter of antimony) with H_2O . $\text{SbCl}_3 + \text{H}_2\text{O}$

= $\text{SbOCl} + 2\text{HCl}$. SbOCl , being insoluble in water, is precipitated. It was formerly called *powder of Algaroth*. SbH_3 is formed whenever a salt of Sb is in contact with nascent hydrogen. Tartar emetic is made by heating cream of tartar, $\text{HKC}_4\text{H}_4\text{O}_6$, with Sb_2O_3 in water. $\text{Sb}_2\text{O}_3 + 2\text{HKC}_4\text{H}_4\text{O}_6 = \text{H}_2\text{O} + 2\text{KSbOC}_4\text{H}_4\text{O}_6$. It is very poisonous and a powerful emetic.

Exp. 293. — Put into a flask about a half a gram of powdered Sb and add 25^{cc} of HCl, then not over a dozen drops of HNO_3 , and heat the mixture till all or most of it dissolves. SbCl_3 forms, and may be tested by pouring a little into water. The rest may be evaporated till it becomes thick.

Exp. 294. — To a solution of SbCl_3 in H_2O and HCl add H_2S solution, or pass H_2S gas into it. The orange precipitate is Sb_2S_3 . It will be recalled that stibnite, Sb_2S_3 , is a black crystalline metallic solid, whereas the Sb_2S_3 obtained is a reddish amorphous powder. They both have the same percentage composition, and may be regarded as allotropic forms of the same compound.

495. Tests. — Each of the above experiments serves as a test for Sb. The sublimate test, however, is the most delicate. This is made exactly the same as Marsh's test for arsenic except that the sublimate of antimony differs from that of arsenic as follows:

ARSENIC.

The sublimate is lustrous and metallic.

It forms beyond the flame and further from it than Sb.

It is more volatile than Sb.

Is soluble in NaClO .

Dissolved in $(\text{NH}_4)_2\text{S}_x$ and evaporated, gives yellow deposit.

ANTIMONY.

The sublimate is black and not lustrous.

It forms on both sides of the flame, and nearer to it than As.

It is less easily driven by heat than As.

Insoluble in NaClO .

Dissolved in $(\text{NH}_4)_2\text{S}_x$ and evaporated, leaves orange deposit.

The sublimate test should be made and each of the above statements verified.

Antimony is distinguished from bismuth by the solubility of SbOCl in hydrogen sodium tartrate, $\text{HNaC}_4\text{H}_4\text{O}_6$, BiOCl being insoluble in it. A mixture of salts of Sb''' and Sn'' may be tested as follows.

Exp. 295. — Pour a little of the solution into HgCl_2 solution, when stannous salts will precipitate HgCl and Hg . Pour more of it into a

Marsh's generator, from which hydrogen is escaping and burning, and decompose the SbH_3 formed with a Bunsen flame (Fig. 166). Try to dissolve the sublimate in NaClO , to distinguish it from As.

496. Uses. — Metallic antimony is used principally in certain alloys, *e.g.*, it makes about 20% of printers' type metal, the rest being either lead, or lead and tin, and it constitutes nearly the same percentage of stereotype metal. Printers' type is used in the setting up of all matter for books and newspapers, books being usually printed from electrotyped (copper plate) material, and papers from stereotyped. Antimony is used in pewter, Britannia metal, white metal, etc. Antimony black is the metal precipitated from SbCl_3 solution by zinc, and is used to give a metallic appearance to plaster casts, etc. Tartar emetic is employed in medicine, and other compounds find use in the chemist's laboratory, and as mordants in calico-printing.

TIN.

497. While not a very abundant nor widely diffused element, tin has a variety of uses by reason of the alloys it forms with many metals, its untarnishability — being one of the least easily corroded of the baser metals — and its easy fusibility and malleability. Tin foil, used for wrappers of various material, is either pure tin or an alloy of tin and lead, the latter being the cheaper. *Tin plate*, used for cans and other ware, consists of sheet iron, which has been cleansed and dipped into molten tin. The tin adheres to the iron, forming a metallic coating which prevents the iron from rusting. The dipping may be done several times and a thicker coating formed.

Terne plate, used for roofing and coarser ware, consists of sheet iron dipped into a mixture of molten tin and lead in varying proportions.

498. History. — This is one of the original ancient metals. It belonged to the bronze age, as explained under copper.

499. Occurrence. — *Cassiterite* (or tin stone), SnO_2 , is the only ore of tin that exists in any quantity, and even this is limited in area. It is found in India (Malacca and Banca), England (Cornwall), and in Saxony. Very little is known to occur in America. The English tin contains a little As and Cu. *Stream tin* is so named because the ore has been washed out by the streams from the rock in which it was formed.

500. Reduction. — The ore, SnO_2 , is crushed and roasted, to remove impurities, then mixed with carbon and strongly heated in a reverberatory furnace (Fig. 170). $\text{SnO}_2 + 2\text{C} = \text{Sn} + 2\text{CO}$.

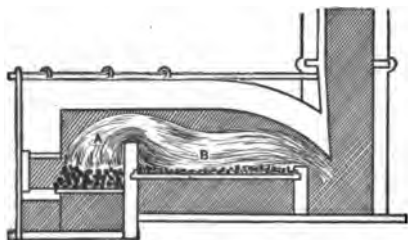


FIG. 170.

501. Properties.

— *Physical.* Soft, malleable, and ductile, tin can be made into foil so thin that 400 sheets will be but a centimeter thick. It is white, crystalline, and the most fusible of common metals. In bending a rod of it, the crystals produce so much friction against each other as to make a sound called the *tin cry*. On etching it with HCl , striations appear, showing its crystalline structure. It fuses at 228° ,

and vaporizes at 1700° . Tin salts are poisonous, the antidote being magnesia.

Chemical. It does not oxidize at ordinary temperatures, but burns with a white light to SnO_2 . It also unites with Cl, Br, I, S, P. There are two classes of salts, the stannous, Sn'' , and the stannic, Sn'''' , the former being more common, the latter more stable. Compare the symbol of its higher oxid, SnO_2 , with CO_2 , SiO_2 , PbO_2 . Tin dissolves in hot HCl , forming SnCl_2 and H_2 . Hot H_2SO_4 forms SnSO_4 and SO_2 . HNO_3 does not dissolve it, but forms insoluble white metastannic acid, $\text{H}_{10}\text{Sn}_5\text{O}_{15}$ (variable). Aqua regia forms SnCl_4 . NaOH acts on tin as follows: $\text{Sn} + 2\text{NaOH} + \text{H}_2\text{O} = \text{Na}_2\text{SnO}_3 + 4\text{H}$. Is Na_2SnO_3 an *ite* or an *ate* salt? Stannous chlorid is readily soluble, is a great reducing agent, and is the chief commercial salt of tin. It reduces HgCl_2 to HgCl and FeCl_3 to FeCl_2 . In solution SnCl_2 is unstable and oxidizes to SnCl_4 and SnOCl_2 by absorption of oxygen.

Exp. 296. — To a little granulated tin in a test tube add HCl . Note the effect, then heat it. Try the same with H_2SO_4 (cautiously) in a porcelain dish. Try to dissolve Sn in HNO_3 . The last reaction is $15\text{Sn} + 20\text{HNO}_3 + 5\text{H}_2\text{O} = 3\text{H}_{10}\text{Sn}_5\text{O}_{15} + 20\text{HNO}$. Wash the residue and try to dissolve it in *aqua regia*.

Exp. 297. — Dissolve Sn in HCl , also in *aqua regia*. Evaporate most of the free acid, and to a part of each solution add H_2S gas, and note the difference. To another part of each add HgCl_2 solution.

Exp. 298. — Oxidize SnCl_2 solution with a little *aqua regia* and add HgCl_2 solution.

502. Alloys. — Tin amalgamates with mercury, and the amalgam is much used for the backs of mirrors. Solder is an alloy of lead and tin, sometimes in about equal parts, at others in varying proportions,

according to what it is desired to solder. Soldering consists in making a surface alloy. Tin is a constituent of fusible metals, and alloys also with iron. Some other alloys are bronze (Sn, Cu, and Zn), Britannia metal (Sn, Cu, Zn, Sb), etc.

503. Tests. — (1) Zinc will deposit tin from a solution. The tin is insoluble in HNO_3 , but soluble in HCl . (2) Brown SnS is thrown down by H_2S from a stannous solution, which is soluble in $(\text{NH}_4)_2\text{S}_x$ or NaOH solution. (3) Adding HgCl_2 solution to a stannous solution forms a white precipitate of HgCl , and if the stannous salt is in excess, a dark gray one of Hg . (4) The salts heated on charcoal give a metallic globule and white incrustation. (5) The *ic* salts of Sn produce similar results, except that HgCl_2 gives no precipitate, and H_2S forms yellow SnS_2 , soluble like SnS . Tin is separated by precipitation by H_2S (from *ous* solutions) as SnS with Hg'' , Pb, Bi, Cd, Cu, As, Sb. From the first five it is separated by dissolving in $(\text{NH}_4)_2\text{S}_x$ (together with As and Sb). From As it may be separated by its solubility in HCl (together with Sb), Sb is removed by Marsh's test, and Sn (precipitated by Zn and Pt) is dissolved in HCl and is tested for with HgCl_2 .

Exp. 299. — Put a piece of Zn into a solution of SnCl_2 and let it stand for some time.

Exp. 300. — Heat for some time B.B.C.C. some SnCl_2 . Notice the incrustation, and examine and test the globule.

Exp. 301. — Make a mixture of solutions of AsCl_3 and SnCl_2 , then precipitate the sulfids with H_2S . Filter, wash the residue, and try to dissolve it in HCl warmed with it some time in a porcelain dish. Filter, and to the filtrate add HgCl_2 solution.

Exp. 302. — Precipitate SnS from SnCl_2 solution, filter, and dissolve the residue in $(\text{NH}_4)_2\text{S}_x$, then add HCl , which throws down the Sn as yellow SnS_2 . The polysulfid of ammonium has oxidized Sn'' to Sn^{iv} .

$$\text{SnS} + (\text{NH}_4)_2\text{S}_x = (\text{NH}_4)_2\text{SnS}_3 + (x - 2)\text{S}. \quad (\text{NH}_4)_2\text{SnS}_3 + 2\text{HCl} = 2\text{NH}_4\text{Cl} + \underbrace{\text{SnS}_2}_{\text{H}_2\text{S}}.$$

504. Uses. — Tin is employed somewhat in sheets, but mainly in alloys, tin and terne plate, foil, etc. SnCl_2 dyers and calico-printers use as a mordant, and chemists use it in the laboratory. SnO_2 is the polishing substance

called putty powder. SnS_2 , under the name of *mosaic gold*, is employed in bronzing. The "purple of Cassius" is an uncertain compound of the chlorids of gold and tin, which imparts to glass a rich purple color after being "fired."

CHAPTER XXXVIII.

BISMUTH, CADMIUM, COPPER.

BISMUTH.

505. The last of the nitrogen group of elements is bismuth, and it differs considerably from the others, all of which form quite well marked acids. Bismuth scarcely forms an acid, its oxids (except the pentoxid, Bi_2O_5 , which is slightly acidic) being of a basic character and neutralizing acids to form salts. It is mainly interesting in forming with other metals alloys of low fusibility, and as a constituent of salts used in medicine.

506. History. — Basil Valentine first mentions bismuth in the last half of the fifteenth century. Pott, 1739, first described its main properties.

507. Occurrence. — Bismuth occurs chiefly in the native state, the largest amount being derived from Saxony. The trioxid, *bismuth ochre*, Bi_2O_3 , and the trisulfid, *bismuthinite*, Bi_2S_3 , are other sources. It is not widely distributed nor abundant, but is often associated in veins with cobalt and silver.

508. Reduction. — Native Bi melts at so low a temperature that it is separated from the earthy material, which is broken up and put into inclined iron cylinders, by heating the mass with charcoal, when the melted metal runs out. The oxid is reduced with carbon. The sulfid

is first roasted, which gives the oxid, and this is treated as before.

509. Properties. — A white metal with a reddish tinge (which distinguishes it from antimony) and a metallic lustre, it is brittle and easily crushed, melts at about 265° , and burns with bluish flame at a red heat to Bi_2O_3 . It alloys with several metals and imparts to the alloy a low fusing-point. Bismuth burns in chlorine, and also combines with other halogens, but not with hydrogen. It is soluble in nitric acid and *aqua regia*, in hot concentrated sulfuric, and but slightly in muriatic. With these it forms respectively $\text{Bi}(\text{NO}_3)_3$, BiCl_3 , $\text{Bi}_2(\text{SO}_4)_3$.

510. Oxids, Bases, Salts. — The only oxid of importance is the trioxid, Bi_2O_3 . Bi_2O_5 is very slightly acidic, the others are basic. Bismuth hydroxid, $\text{Bi}(\text{OH})_3$, is a white, flaky, insoluble solid, made by adding the hydrate of sodium or ammonium to a soluble bismuth salt. $\text{BiCl}_3 + 3\text{NaOH} = \text{Bi}(\text{OH})_3 + 3\text{HCl}$. Bismuthyl hydrate, or basic bismuth hydrate, is BiOOH . The important salts are the chlorid, BiCl_3 , oxychlorid, BiOCl , subnitrate (also called basic nitrate and oxynitrate), BiONO_2 (variable), and the subcarbonate (or basic carbonate), $(\text{BiO})_2\text{CO}_3$. The last two are used much in medicine as a remedy for dysentery, cholera, etc. They are insoluble. The subnitrate is made by pouring into water some of the normal nitrate dissolved in HNO_3 : (1) $\text{Bi}(\text{NO}_3)_3 + 2\text{H}_2\text{O} = \text{Bi}(\text{OH})_2\text{NO}_3 + 2\text{HNO}_3$; (2) $\text{Bi}(\text{OH})_2\text{NO}_3 = \text{BiONO}_2 + \text{H}_2\text{O}$. The quantity and temperature of the water and the amount of free acid present vary the reaction.

511. Tests. — (1) The salts of bismuth are distinguished by their forming white basic precipitates (especially the chlorid) when poured into water; (2) From antimony, whose salts react similarly with H_2O , it is distinguished by forming a black precipitate of Bi_2S_3 with H_2S , whereas salts of the former give an orange-red precipitate which is soluble in $(\text{NH}_4)_2\text{S}_x$, ammonium polysulfid; (3) Bismuth oxychlorid, BiOCl , also is insoluble in primary sodium tartrate, $\text{HNaC}_4\text{H}_4\text{O}_6$, solution, while SbOCl is dissolved by it. B.B.C.C. salts of Bi give a yellow incrustation and

metallic globule which is brittle ; (4) From salts of Cu and Cd it is separated by addition of NH_4OH , in excess, which precipitates white, flaky $\text{Bi}(\text{OH})_3$.

Exp. 303. — Melt in an iron ladle 4s bismuth, 2s lead, 2s tin, and 1s cadmium. Pour the molten mixture into an evaporating dish and let it cool. When it is hardened pour boiling water over it or surround the containing vessel with hot water.

Exp. 304. — Boil a small piece of bismuth in nitric acid diluted with half its volume of water. When the action stops pour a few drops of the solution into water in a test tube. If no precipitate forms set it aside. In case there was too much free acid it will form slowly or not at all. In that case concentrate the original solution by evaporation.

Exp. 305. — Dissolve bismuth in *aqua regia* and add a few drops to some water, as above. This is the best test for bismuth. To apply it to any other salt than the chlorid first acidify the salt with HCl . $\text{BiCl}_3 + \text{H}_2\text{O} = \underbrace{\text{BiOCl}} + 2\text{HCl}$.

Exp. 306. — Pour hydrogen sulfid solution (or use H_2S gas) into a solution of bismuth chlorid obtained as above.

Exp. 307. — Try the action of NH_4OH on separate solutions of BiCl_3 , CdCl_2 , and CuCl_2 . Again try the action of NH_4OH on mixtures of the three solutions and separate the first by filtration.

Exp. 308. — Heat B.B.C.C. in the reducing flame, some solid compound of Bi, observing finally the incrustation and the globule. Try to crush the latter, then dissolve it in HNO_3 .

512. Uses. — The element is utilized for casts, medals, seals, and in alloys of various fusible metals. Its compounds are employed in medicine and for coloring glass and porcelain, for calico-printing, etc.

For the purpose of comparison, the following table of the nitrogen group of elements (see Meyer's Table, p. 199) is appended. Note the similarity of valence ; also that of the composition in compounds of the different elements, which strikingly illustrate the Periodic Law.

THE NITROGEN FAMILY.

The following are the compounds of members of the nitrogen family with oxygen, hydrogen, chlorine, and some typical acids and salts.

ELEMENTS.	WITH O.	WITH H.	WITH CL.	WITH H AND O.	WITH K AND O.
N'-v	N ₂ O NO N ₂ O ₃ N ₂ O ₄ N ₂ O ₅	NH ₃	NCl ₃	HNO ₂ HNO ₃	KNO ₂ KNO ₃
P''', v	P ₂ O ₃ P ₂ O ₅	PH ₃	PCl ₃ PCl ₅	H ₃ PO ₃ H ₃ PO ₄	K ₃ PO ₃ K ₃ PO ₄
As''', v	As ₄ O ₆ As ₂ O ₅	AsH ₃	AsCl ₃	— H ₃ AsO ₄	K ₃ AsO ₃ K ₃ AsO ₄
Sb''', iv, v	Sb ₄ O ₆ Sb ₂ O ₄ Sb ₂ O ₅	SbH ₃	SbCl ₃ SbCl ₅	— H ₂ Sb ₂ O ₅ H ₃ SbO ₄	— K ₂ Sb ₂ O ₅
Bi''-v	Bi ₂ O ₂ Bi ₂ O ₃ Bi ₂ O ₄ Bi ₂ O ₆	—	Bi ₂ Cl ₄ BiCl ₃	Bi(OH) ₃ HBiO ₃	

CADMIUM.

513. *Cadmium*, discovered by Stromeyer in 1817, is not an important element, nor abundant. It is commonly found associated with zinc, and as *greenockite*, CdS. In chemical properties these two metals resemble each other. Like zinc it is obtained from the ore by first roasting, forming CdO, from which Cd is obtained by distillation, with carbon as a reducing agent. It is a little more volatile than zinc, hence the first

portion of the distillate is separated as cadmium. It is a white metal which forms a constituent of several alloys that have a low fusing temperature. It readily forms amalgams which are at first soft and then harden. Hence its use in filling teeth.

Cadmium is soluble in the common acids. In analysis it is separated from copper salts (*e.g.*, CuCl_2 and CdCl_2) by KCN solution, excess of which forms and dissolves potassium cadmic cyanid, $\text{K}_2\text{Cd}(\text{CN})_4$, and potassium cuprous cyanid, $\text{K}_3\text{Cu}(\text{CN})_4$. H_2S precipitates CdS, but not CuS, from the mixed solutions. HCl with H_2S will throw down CuS. CdS is used as a pigment.

Exp. 309. — Mix solutions of CuCl_2 and CdCl_2 and saturate with H_2S . Dissolve in dilute HNO_3 , with heat, alkalize with NH_4OH , and add KCN solution till the blue color disappears. Saturate with H_2S , filter, and add HCl to the filtrate.

Like other members of the copper group Cd is thrown out of solution by H_2S , CdS being formed. CdS and As_2S_3 are both bright yellow and are precipitated by H_2S . The former is insoluble in ammonium polysulfid, $(\text{NH}_4)_2\text{S}_x$, the latter is soluble.

Exp. 310. — Warm separate precipitates of CdS and As_2S_3 (obtained by H_2S on CuCl_2 and AsCl_3) with $(\text{NH}_4)_2\text{S}_x$.

COPPER.

514. Next to iron probably copper is now the most useful of metals. It is ductile, it does not readily oxidize, and it is almost as good a conductor of electricity as silver is, for which reasons it is used for telegraph, telephone, and trolley wires. The ores of copper are very abundant and widely distributed. A single mine in this country has produced more than 50,000,000 pounds of copper a year, while in one month the United States has smelted above 20,000 tons. One mine, the Tamarack, in the Lake Superior region, has a depth of nearly a mile.

515. History. — Copper was one of the earliest known metals, being found alloyed with tin in the implements of the bronze age, before

the use of iron. Some of the Lake Superior mines have been worked for half a century, and evidence is found that prehistoric man dug copper there.

516. Occurrence. — This element occurs both free and in compounds. In the free state it is either crystalline or amorphous, and occurs thus in Michigan, China, Japan, Sweden. The compounds are mainly sulfids, as *chalcopyrite*, CuFeS_2 , and *chalcocite*, Cu_2S . *Cuprite* is Cu_2O , and *malachite*, $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$. The chief producers of copper are the United States (Montana and Michigan leading), Chile, and Spain. The Lake Superior mines are the most important that furnish the element in its native state. Here it occurs in a conglomerate rock.

517. Reduction. — When copper occurs uncombined it has to be separated from the admixture of rock — a crushing process done by “stamp-mills.” The oxid ores are reduced with carbon, the copper being melted at 1150° . Sulfid ores are roasted, thus changing a part into the oxid, *e.g.*, Cu_2O , and leaving the rest as sulfid, Cu_2S . The difficulty lies in changing all the sulfid to oxid. These ores usually contain some combined iron, to remove which silica is added in the furnace. Thus is formed and separated a slag of silicate of iron. There are left copper and iron sulfids, the mixture being called *matte*. The *matte* is again heated with carbon and silica. Some copper is reduced each time, and some by the action of the oxid on the sulfid, *e.g.*, $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} = 6\text{Cu} + \widetilde{\text{SO}_2}$. A great deal of copper is now reduced by electrolytic processes.

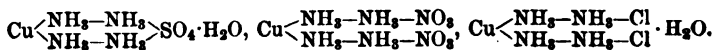
518. Properties. — *Physical.* This is a red metal, malleable, ductile, tenacious, and is a good conductor of

heat and electricity. It vaporizes only in the oxy-hydrogen flame. Copper salts are poisonous, though not now regarded so poisonous as formerly. The antidote is white of egg, or milk.

Chemical. Cu does not oxidize in dry air unless heated to redness, when it forms CuO. In moist air it becomes after a time covered with a brown oxid or a green carbonate. Air or water containing NaCl coats it with green CuCl_2 . It has great affinity for Cl, though HCl acts on it but slightly. HCl would tend to form the lower chlorid, CuCl , and this is insoluble. *Aqua regia* readily dissolves copper to CuCl_2 , which may also be made from the carbonate and HCl.

519. Compounds. — Copper has two valences, 1 and 2. The univalent compounds are comparatively unimportant, except Cu_2O and Cu_2S . CuCl is a valuable reagent in gas analysis. The divalent ones, *e.g.*, CuCl_2 , $\text{Cu}(\text{NO}_3)_2$, are common. The best solvent of the metal is HNO_3 . $3\text{Cu} + 8\text{HNO}_3 = 3\text{Cu}(\text{NO}_3)_2 + 4\text{H}_2\text{O} + 2\widetilde{\text{NO}}$. Hot H_2SO_4 also dissolves it. $\text{Cu} + 2\text{H}_2\text{SO}_4 = \text{CuSO}_4 + 2\text{H}_2\text{O} + \widetilde{\text{SO}_2}$. The nitrate, sulfate, and chlorid are all soluble, and from them the insoluble salts may be made by precipitation. Sulfate of copper crystallizes (as blue vitriol) with 5 molecules of water, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Heated to 100° it loses 4 molecules, and at 200° the last H_2O is separated, and the crystal becomes a white powder. For Paris or Scheele's green, see Arsenic.

Ammonia forms with solutions of copper salts a great variety of deep blue cuprammonium salts, as



520. Alloys. — Copper forms various alloys, as bronze (Cu, Zn, Sn), brass (Cu, Zn, with usually a little Pb), German silver (Cu, Zn, Ni), Dutch metal (Cu, Zn), gun and bell metals (Cu and Sn), Talmi gold (Cu, Al).

521. Tests and Separations. — (1) Most salts of copper are green or blue; (2) The addition of NH_4OH in excess intensifies the blue color, as explained above; (3) Volatile Cu salts impart a green or blue color to the Bunsen flame; (4) With hydrogen sulfid they give a black precipitate of CuS ; (5) $\text{K}_4\text{Fe}(\text{CN})_6$ gives a red-brown precipitate of $\text{Cu}_2\text{Fe}(\text{CN})_6$; (6) Na_2CO_3 when heated with the salts gives metallic Cu; (7) Zinc precipitates Cu from a solution, replacing the Cu, *e.g.*, $\text{CuSO}_4 + \text{Zn} = \text{ZnSO}_4 + \text{Cu}$; (8) In analysis it is separated from Cd — after the removal of Hg, Pb, Bi — by adding KCN, as mentioned under Cd. H_2S then precipitates only Cd. When this is removed HCl throws down CuS .

Exp. 311. — Try to dissolve copper in HCl. Try to dissolve it in HNO_3 mixed with half a volume of water. Try to dissolve it in strong H_2SO_4 . Use heat, if necessary, in each case. Try *aqua regia*. Dip a splint into the *aqua regia* solution and hold it in the flame.

Exp. 312. — Mix some copper salt with dry Na_2CO_3 and fuse it strongly B.B.C.C.

Exp. 313. — To the solution of a copper salt add H_2S . To another solution add $\text{K}_4\text{Fe}(\text{CN})_6$ solution.

Exp. 314. — Add very little NH_4OH to a solution of $\text{Cu}(\text{NO}_3)_2$ or CuCl_2 . $\text{Cu}(\text{OH})_2$ is precipitated. Now add excess of NH_4OH and shake it. To part of this add KCN solution till the color disappears, then add H_2S and finally HCl. To the other part add H_2S at once.

CHAPTER XXXIX.

LEAD, SILVER, MERCURY, GOLD, PLATINUM.

LEAD.

522. The compound called *white lead* is the basis of white paint, and has been known for thousands of years. Up to the present time its manufacture has undergone little change. It was originally made from lead, vinegar, and carbon dioxid, even before the Christian era. Other colored salts of lead are used for various pigments, as *chrome yellow*, which is chromate of lead.

523. History.—Lead is one of the seven original metals of the ancients. They named it *Saturn*, and supposed that the planet of that name had a benign influence upon it. Poisoning by lead salts was called *saturnine poisoning*.

524. Occurrence.—The element is very rarely found free. Its principal ore is *galenite* (or *galena*), PbS , which much resembles the element. *Cerussite*, PbCO_3 , is another ore, and *anglesite*, PbSO_4 , is found in some places, notably in Australia. Lead, in its ores, is one of the most abundant of metals in almost every country. In the United States the central and western portions furnish the most. It is usually mixed with a small percentage of silver, and often associated with zinc, barium sulfate, etc.

525. Reduction.—This, as regards *galena*, involves two processes. In the first the ore is roasted in a rever-

beratory furnace (p. 280) with plenty of air. The ore is constantly stirred in the furnace. SO_2 is formed and liberated, and some of the lead is oxidized to PbO , some to PbSO_4 , while a part of the PbS remains unchanged.



In the second process air is excluded, and the partially reduced products are subjected to greater heat. The oxygen and sulfur then pass off as SO_2 and leave the lead.



Another method of reduction consists in heating the ore with iron, which combines with the sulfur.



The method of separating silver from argentiferous lead ore is described under Silver.

526. Properties. — *Physical.* Lead is a bluish white metal, so soft as to be scratched with the finger nail, and to leave a black mark on paper. It has little tenacity, but can be drawn into wire and rolled into sheets, in fact it is the least tenacious and softest of the common metals. The specific gravity is 11.4, and it melts as low as 325° . To these properties are due its uses.

Chemical. It oxidizes quickly when exposed to air, becoming coated with the suboxid, Pb_2O . With water, air, and carbon dioxid, PbCO_3 is formed. Pure water acts but little on it, but the presence of organic matter hastens its activity. Heated with access of air it forms the monoxid, PbO (called *litharge*), or with more heat and for a longer time Pb_3O_4 , *red lead*. If heated too strongly, it again becomes PbO . The best solvent of Pb is nitric

acid, with which it forms $\text{Pb}(\text{NO}_3)_2$. As the latter is insoluble in strong HNO_3 , the dilute acid should be used (specific gravity 1.2). Pb also dissolves in acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, to form $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. Neither HCl nor H_2SO_4 , unless concentrated, acts very much on the metal. HCl forms a surface coating of PbCl_2 , and hot H_2SO_4 forms and dissolves some PbSO_4 . The nitrate and the acetate are the principal soluble salts of lead. PbCl_2 is slightly soluble in cold water, readily so in boiling water, from which it crystallizes in needles as the water cools.

All salts of lead soluble in the fluids of the body are poisonous and cumulative. They seem to have affinity for the albuminoids, and hence are slowly eliminated from the body. A solution of magnesium sulfate, MgSO_4 , is the antidote. It forms insoluble PbSO_4 . KI also is used.

527. Compounds. — There are five oxids, viz., Pb_2O , PbO , Pb_2O_3 , Pb_3O_4 , PbO_2 . Of these PbO , litharge, and Pb_3O_4 , red lead or minium, are most important. Red lead is somewhat variable in composition, and is thought to be composed of $2\text{PbO} + \text{PbO}_2$. Boiling red lead with HNO_3 removes the former and leaves brown PbO_2 . Both PbO and Pb_3O_4 are used in the manufacture of flint glass, which Pb makes soft and highly refractive to light. This glass is used for lenses, cut-glass ware, and gems. The compound formed is lead silicate. Pb_2O is made by heating lead oxalate, PbC_2O_4 . Most salts of lead are insoluble, and are made by precipitation from the nitrate or acetate, e.g., H_2S forms PbS , HCl forms PbCl_2 , $\text{K}_2\text{Cr}_2\text{O}_7$ forms PbCrO_4 , KI forms PbI_2 . NaOH dissolves the greater number of these salts of lead. Lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, is a sweet, astringent salt, used somewhat in medicine.

528. White Lead. — This substance is a basic carbonate of varying composition, e.g., $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$. Ground and suspended in linseed oil it forms white paint. The main process employed up to the present time for its manufacture is known as the *Dutch process*, and takes four to six months for its completion. It consists in forming the acetate of lead, and from that the carbonate. Perforated sheets of lead called *buckles* are placed in pots, above but not in contact with acetic

acid, $\text{HC}_2\text{H}_3\text{O}_2$ (Fig. 171). Successive layers of these pots are arranged in a shed, each tier separated from the one above by boards covered with tan bark, or other fermenting material (Fig. 172), which serves first to warm the acid and thus aid the chemical action, second, to change the acetate formed to the sub-acetate, and finally, to furnish CO_2 to change the latter into the basic carbonate. The acetic acid fumes attack the lead and cover it with acetate of lead, which is

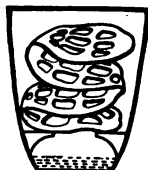


FIG. 171.

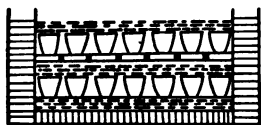
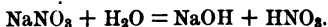


FIG. 172.

changed to basic acetate, and then transformed to basic carbonate. When the process is complete, the white product is removed from any remaining lead, washed, and ground with oil, when it is ready for use.

Electrolytic White Lead. A process has recently been patented for making white lead by electrolysis of NaNO_3 —which gives NaOH and HNO_3 .



A bar of lead is placed at the electrode where the acid is liberated. The latter attacks the lead, forming $\text{Pb}(\text{NO}_3)_2$. The NaOH solution, formed at the other electrode, is drawn off separately, and the two solutions, $\text{Pb}(\text{NO}_3)_2$ and NaOH , are mixed in proportionate quantity, giving rise to $\text{Pb}(\text{OH})_2$. $\text{Pb}(\text{NO}_3)_2 + 2\text{NaOH} = \text{Pb}(\text{OH})_2 + 2\text{NaNO}_3$. The nitrate of sodium is used again, as at first. $\text{Pb}(\text{OH})_2$ is now mixed with Na_2CO_3 or HNaCO_3 , when this reaction ensues: $\text{Pb}(\text{OH})_2 + \text{Na}_2\text{CO}_3 = \text{PbCO}_3 + 2\text{NaOH}$, giving the final product, carbonate of lead. By passing CO_2 into NaOH , HNaCO_3 is produced, and thus each by-product is used again.

Exp. 315. — Heat for several minutes B.B.C.C. in the oxidizing flame a piece of lead half the size of a pea. Notice any yellow vapor, and a yellow coating of PbO on the charcoal.

Exp. 316. — Mix 1 or 2s of lead monoxid, PbO , with $\frac{1}{4}$ the amount of saltpetre, KNO_3 , or chlorate of potash, KClO_3 , and heat in an iron dish or spoon. *Red lead* forms, as the result of oxidation.

Exp. 317. — Put into an evaporating dish or test tube 1 or 2s of red lead, Pb_3O_4 , cover it with dilute HNO_3 , and boil it. A brown insoluble

residue, PbO_2 , is left. Filter the solution, dilute it, and test with H_2S , H_2SO_4 , etc.

Exp. 318.—Try to dissolve a small fragment of lead in dilute HNO_3 (one-third acid, two-thirds water). Warm it to start the action. When action stops, remove any undissolved Pb, evaporate the liquid. Finally add water and obtain a solution for testing. Try to dissolve PbO or PbCO_3 in dilute HNO_3 .

Exp. 319.—Try to dissolve Pb in acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$. Filter, and test the solution with H_2S . Try to dissolve lead in HCl . Also in H_2SO_4 .

Exp. 320.—Put a piece of zinc or a zinc wire into a solution of $\text{Pb}(\text{NO}_3)_2$, and watch the result.

529. Tests and Separations.—Lead is distinguished from other metals, except silver and mercury (ous), by the slight solubility of its chlorid—precipitated from solutions by HCl —in cold water, and from those two elements by its solubility in hot water, from which it is again thrown down by (1) H_2S as PbS (black), (2) $\text{K}_2\text{Cr}_2\text{O}_7$ as PbCrO_4 (yellow) (3) H_2SO_4 as PbSO_4 (white), (4) on cooling as PbCl_2 (needle-shaped crystals). PbCl_2 is slightly soluble in cold water. NH_4OH dissolves AgCl and blackens HgCl , but does not dissolve, or change the color of, PbCl_2 .

H_2S is the best test for lead, of which it will detect $\frac{1}{100000}$ part in solution. Another test is the formation of PbI_2 —with KI solution and a salt of Pb in solution. The precipitate is somewhat soluble in boiling H_2O , from which it crystallizes in golden yellow plates, as it cools.

Exp. 321.—Take three test tubes. Into one pour 3 or 4^{cc} of $\text{Pb}(\text{NO}_3)_2$ solution, into another AgNO_3 solution, into the third HgNO_3 solution. Add a little HCl to each. Now add NH_4OH , and shake them. Finally add cautiously HNO_3 .

Exp. 322.—Obtain PbCl_2 by adding HCl to 3 or 4^{cc} of $\text{Pb}(\text{NO}_3)_2$. Dilute it, boil the liquid, and filter, if all is not dissolved. To part of the filtrate add H_2S , to another part H_2SO_4 . Let another part cool.

Exp. 323.—To 5^{cc} of H_2O in a test tube slowly add an equal volume of commercial H_2SO_4 . The white precipitate is PbSO_4 . Explain.

Exp. 324.—Precipitate PbI_2 from $\text{Pb}(\text{NO}_3)_2$ and KI . Decant, and pour over the residue some H_2O , then boil, and let it cool in a test tube.

530. Uses. — Lead is used for water-pipes, linings for sulfuric-acid chambers, for shot, bullets, alloys, and various salts of the metal. A ton of lead for shot is mixed with about 40 pounds of arsenic, for hardening. The molten mixture runs through a perforated holder at the top of a high tower and falls into water. If the shot are elongated, too little As was used; if flattened, too much. The chief alloys of lead are type metal (Pb and Sb), solder (Pb and Sn), and tin foil (Sn and Pb). Some foil has only Sn. *Terne plate* is iron coated with a mixture of Sn and Pb. This is employed to cover roofs of houses. PbO and Pb_3O_4 are used in glass-making, Pb_3O_4 in matches, in sealing-wax, and in painting iron. A great deal of lead goes to make paint, and some hair dyes contain its salts. The sulfur in the hair forms and deposits PbS , which is black.

SILVER.

531. Of all metals silver is the most brilliantly white, and the best conductor of electricity and heat. It is one of the few that does not oxidize, even in moist air or at any temperature. On account of its brilliancy and permanency it has always been used for jewelry and as a medium of exchange. It has more insoluble salts than any other metal, and on many of these light has a peculiar action, for which reason they form the basis of photography.

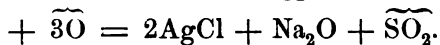
532. History. — Silver was one of the seven metals of the ancients, and has been known from the earliest times. By the alchemists it was called *Luna*, and was represented by the crescent moon. During the age of Pericles some 20,000 slaves were employed in the silver mines of Greece.

533. Occurrence. — A mass weighing quarter of a ton has been found native, but the uncombined state is not its common habit of occurrence. The more usual ore is *argentite*, Ag_2S , and it is generally intimately mixed with the lead ore, *galenite*, PbS . There are many other mineral compounds of silver, such as *pyrargyrite*, Ag_3SbS_3 , and *horn silver*, AgCl — in all 24 species. Mexico, South America, Colorado, Nevada, the Hartz mountains, Australia, and India furnish great quantities of the white metal. The world's product amounts to hundreds of millions of dollars' worth per annum, of which the United States furnishes more than any other country. The richest mine of modern times was the Comstock lode of Nevada, now worked out.

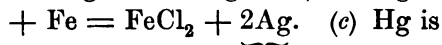
534. Metallurgy. — Of the many methods for reducing silver from its ores two especially merit our consideration. (1) *Pattinson's process*, (2) *the amalgamation process*. The richness and kind of ore, its location, the cost of labor, etc., determine which process shall be used. The greatest amount of the world's silver is obtained by the amalgamation process. (1) In the Pattinson method the problem is to separate the Ag from Pb, each occurring intimately mixed as Ag_2S and PbS . The sulfur is eliminated as described under Lead, leaving Ag and Pb. These are melted together and allowed to cool, when the nearly pure lead crystallizes on the surface and is skimmed off with a perforated ladle. Another growth of crystals is treated in the same way, until finally the residue in the basin is nearly all silver. The remaining portions of lead are then oxidized by melting the residue in a cupel and blowing air across it. The lead is oxidized

and removed from the surface, and the silver not being affected by oxygen, is left in the bottom as a brilliant bead. (2) There are several parts to the amalgamation process, sometimes more than others.

(a) The ore is ground, mixed with NaCl, and roasted. $\text{Ag}_2\text{S} + 2\text{NaCl}$



(b) The AgCl is then mixed with scrap iron and water (often in a revolving drum, Fig. 173). 2AgCl



(c) Hg is then introduced to absorb (or amalgamate) the Ag, as water would

absorb sugar. (d) The Ag is separated from Hg by distilling the latter.

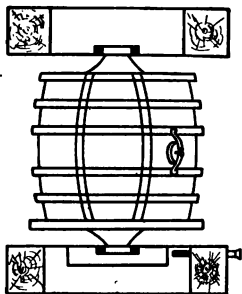


FIG. 173.

A modification of this process consists in mixing an impure CuSO_4 (made by roasting chalcopryrite, CuFeS) with NaCl and the ore. $\text{CuSO}_4 + 2\text{NaCl} = \text{CuCl}_2 + \text{Na}_2\text{SO}_4$. $2\text{CuCl}_2 + \text{Ag}_2\text{S} = 2\text{CuCl} + \text{AgCl} + \text{S}$. Hg is added, which forms the amalgam, and is separated as before.

535. Properties. — *Physical.* Silver is very white, takes a high polish, and is almost as heavy as lead (specific gravity 10.5). Next to gold it is the most ductile and malleable of metals, and ranks a little higher than copper or any other metal as a conductor of heat and electricity. It melts at about 1000° , can be distilled with great heat, and volatilizes in the electric furnace. It is not as hard as copper, but harder than gold. Hence in coins and silverware a small per cent of copper is used.

Sterling silver has $7\frac{1}{2}\%$, United States mint silver 10%. Its only important alloys are those with copper, — others, such as Zn, Sn, and Bi alloys, being brittle. It readily forms amalgams, two of which, Hg_2Ag and Hg_3Ag , are definite compounds and found native. Silver salts are poisonous, the antidote being NaCl solution.

Chemical. Silver does not combine with oxygen (except with ozone) at any temperature, not even when moist, but when melted it begins to absorb (or occlude) oxygen, sometimes occluding twenty times its volume. When the metal solidifies, the gas is liberated with explosions — called spitting — an effect like minute volcanoes. Ozone forms with the metal an oxid, perhaps Ag_2O_2 . Ag_2O is formed from solution, a fixed alkali acting on AgNO_3 . Alkalis do not act on the metal, hence dishes and moulds of Ag are employed by workmen and analysts in NaOH, etc. Ag combines readily with sulfur, hydrogen sulfid, etc., to form Ag_2S . “Oxidized silver” is made by immersing the metal in potassium polysulfid, K_2S_x , the brown part being Ag_2S . Eggs, mustard, etc., tarnish spoons by reason of the sulfur they contain, and coins are sulfurized by the S in perspiration. Silver is but slightly acted on by HCl, but is dissolved by HNO_3 (somewhat diluted), and by hot H_2SO_4 , forming AgNO_3 and Ag_2SO_4 .

536. Compounds. — The most important silver salt and the only common soluble one is AgNO_3 , and from it other salts are made. Most of these salts, if in contact with organic matter, blacken when exposed to the light. Carbon and its compounds in this way appear to reduce the salts, depositing either Ag or some compound of it. This is the cause of the blackening of the photographer's

hands. The deposit can be removed by a solution of KI or of KCN. Thickened with a gum, AgNO_3 solution is the basis of indelible ink, Ag being deposited in the fiber of the inscribed cloth. Hair dyes also often contain this salt. *Lunar caustic* is a form of AgNO_3 —made by fusing and running it into moulds—which is used by surgeons to cauterize the flesh. The chlorid and bromid, AgCl and AgBr , are most affected by light, and are hence the basis of photography. Most of its salts are soluble in NH_4OH , $\text{Na}_2\text{S}_2\text{O}_3$, or KCN. Silver plating on a base metal, as white metal, is done with a solution of AgNO_3 and KCN.

Exp. 325.—Pour over a ten-cent silver coin in an evaporating dish about 2^{cc} of HNO_3 (half water), and warm it till action begins, then remove the lamp. When the action stops, add water, pour the liquid into a test tube, and put a copper wire into it. Remove the deposit, wash it, and dissolve it in dilute HNO_3 . Finally evaporate the liquid, and dissolve the residue in water for a stock solution.

Exp. 326.—Test the action of HCl , also of H_2SO_4 , and then of aqua regia on a silver coin.

537. Tests.—(1) AgCl is one of only three insoluble chlorids, and is the only one of the three which is soluble in NH_4OH , and from which it is re-precipitated by HNO_3 . (2) AgCl exposed to light first turns pink, then brown and black. Metallic silver is probably deposited. (3) Zn, Cu, etc., will deposit metallic Ag from a solution of its salts. (4) Tartrates, with a soluble salt of Ag slightly alkalized with NH_4OH and heated, give a metallic mirror. (5) With $\text{K}_2\text{Cr}_2\text{O}_7$ solution AgNO_3 gives a red precipitate of Ag_2CrO_4 . (6) It reduces to a white malleable bead without an incrustation on treatment with Na_2CO_3 , before the blowpipe.

Exp. 327.—Add dilute HCl to some AgNO_3 solution. When the white precipitate subsides, pour off most of the supernatant liquid, and add just enough NH_4OH to dissolve the residue, then acidify with HNO_3 .

Exp. 328.—Prepare some AgCl , as above, filter it, and expose the residue to direct sunlight for some time. With a stirring rod dipped in

AgNO_3 solution write on a sheet of paper, and expose the latter to the sun's rays.

Exp. 329. — Place a clean copper wire or a strip of zinc in a solution of AgNO_3 , and after a time remove, carefully wash, and with the microscope examine any deposit.

Exp. 330. — To 5^{cc} of H_2O in a test tube add half a dozen drops of NH_4OH , shake it, then add just enough AgNO_3 solution to leave a precipitate on shaking, then filter, and to the filtrate add a very few drops of $\text{HNaC}_4\text{H}_4\text{O}_6$ or other tartrate. Place the tube in a receiver or larger tube of hot water. A metallic mirror of silver will collect on the sides of the tube.

Exp. 331. — Mix solutions of $\text{K}_2\text{Cr}_2\text{O}_7$ and AgNO_3 . The red precipitate is Ag_2CrO_4 .

Exp. 332. — Powder a small crystal of AgNO_3 , and mix with twice its bulk of dry Na_2CO_3 . Fuse it B.B.C.C. for some time. See whether there is any incrustation, and test the malleability of the bead.

538. Uses. — Solid silver (alloyed, as described) and silver plate are much in use for table ware, and for ornaments, watches, etc. All civilized countries have minor coins of silver, and the amount in circulation is enormous. Bullion is sold in ingots of 100 pounds each. Some is used in silvering reflectors and mirrors. Its salts are employed in electroplating, in photography, surgery, hair dyes, indelible inks, chemical analysis, etc.

PHOTOGRAPHY.

539. History. — The sixteenth-century alchemists knew that silver chlorid was blackened by sunlight. Scheele, 1777, found that chlorin was set free from silver chlorid by the action of light. Ritter, 1801, found that red rays do not affect AgCl . Herschel, 1836, found that sodium thiosulfate would dissolve such parts of silver chlorid as had not been affected by light. Not to mention a multitude of other discoveries before and since, Daguerre, 1839, found a substance which would render visible and permanent the "invisible image" impressed on silver iodid by sun-

light. Thus—by finding a developer—he invented the first photographic process. The pictures, which in some respects were the most perfect ever made, were called *Daguerreotypes*.

540. The Process.—The silver halids, AgCl , AgBr , AgI , are very sensitive to certain light rays, most so to violet, but red rays do not affect the salts; hence, in the “dark room,” light is admitted only through ruby glass. Photography involves two processes. The negative of the picture is first taken upon a prepared plate of glass or other material, and from this the positive is printed on prepared paper. The negative shows the lights and shades reversed, while the positive gives objects their true appearance.

541. The Negative.—Plates for negatives are prepared as follows: The glass is carefully covered on one side with an emulsion of gelatin and AgBr , making what is called gelatin-bromid plates. This is done in a room dimly lighted with ruby light, and the plates are dried and packed in sealed boxes. The artist opens them in his dark room, inserts the plates in holders with the film side out, covers them with a slide, adjusts to the camera, previously focused, and makes the exposure to light, the time of which varies with the intensity of light, the kind of plate, and the lens, from several seconds, minutes, or hours, to a very small fraction of a second. As short as $\frac{1}{5000}$ part of a second has been claimed for some instantaneous work.

In the dark room the plates are removed, and can at once be developed, or may be kept for some time in darkness before developing. No change appears in the plate until the picture is developed, though the light has done its work. Just what part this light plays is uncertain, but it is supposed to change AgBr to Ag_2Br . $2\text{AgBr} = \text{Ag}_2\text{Br} + \widehat{\text{Br}}$. To “develop” the negative the plate is put into some solution such as pyrogallic acid mixed with sodium carbonate.

Here again the action is somewhat obscure, but those parts of the film which were affected by light are made visible, a part at least of the Ag_2Br being reduced to metallic silver, and left as a black deposit. $\text{Ag}_2\text{Br} = 2\text{Ag} + \text{Br}$. Thus the part which was light in the original, is dark in the negative. The AgBr not affected by the light, is left white and unchanged by the developer, and the next process, called “fixing,” consists in dissolving it. For this process a solution of sodium thiosulfate (hyposulfite or hypo), $\text{Na}_2\text{S}_2\text{O}_3$, is used. $2\text{AgBr} + 3\text{Na}_2\text{S}_2\text{O}_3 = \text{Ag}_2\text{Na}_4(\text{S}_2\text{O}_3)_3 + 2\text{NaBr}$. Both products are dissolved, and the plate contains silver deposited on certain parts of the gelatin, most where the light was strongest, least where weakest.

542. The Positive. — Paper is covered on one side with a film of albumen, and is floated, film side down, on a solution of NaCl ; it is then dried, when a thin layer of NaCl covers the surface. Again it is floated, film side down, on a solution of AgNO_3 , when this reaction takes place: $\text{NaCl} + \text{AgNO}_3 = \text{AgCl} + \text{NaNO}_3$. When dried, the albumen holds a deposit of AgCl . The sensitized paper is then placed under a negative, film to film, in a printing frame, and exposed to sunlight for a longer or shorter time. What is dark in the negative will be light in the positive (as sunlight cannot penetrate the parts over which is a deposit of silver), and *vice versa*. $2\text{AgCl} = \text{Ag}_2\text{Cl} + \widehat{\text{Cl}}$. Also $\text{AgCl} = \text{Ag} + \widehat{\text{Cl}}$. After printing, the picture is *toned* and *fixed*. Toning consists in giving it a rich color by replacing part of the Ag_2Cl with gold from a solution of AuCl_3 . $3\text{Ag}_2\text{Cl} + \text{AuCl}_3 = 6\text{AgCl} + \text{Au}$. Fixing removes the unaffected AgCl , as in the negative, $\text{Na}_2\text{S}_2\text{O}_3$ solution being used as before. After thorough washing the picture can be mounted. In fine portrait work, both negative and positive have blemishes removed with India ink or colored pencils, a process called “retouching.”

MERCURY.

543. Of all known elements, but two are distinctly liquid at ordinary temperatures. Mercury is the only liquid metal. Its vapor weighs one hundred times more than hydrogen. With almost every metal it forms an alloy which is called an *amalgam*. With iron or platinum it will not unite, but it amalgamates even with sodium, potassium, and ammonium. It is used very largely in mining to dissolve gold and silver, by forming with them amalgams, from which it is separated by distillation.

544. History. — It is one of the metals known to the ancients, and was named from the planet Mercury. Another name is quicksilver (or liquid silver) from its resemblance to the latter metal in permanence and untarnishability.

545. Occurrence. — The main mercury compound which occurs in nature is cinnabar, HgS ; the element occurs free, but only in very small particles. The compound

is not widely distributed nor abundant. Idria in Austria, Almaden in Spain, and New Almaden in California are the three main sources of supply. Mexico, Peru, and China also have mines of it.

546. Reduction. — Cinnabar is very easily reduced by roasting it in a furnace (*A, B*, Fig. 174) which is con-

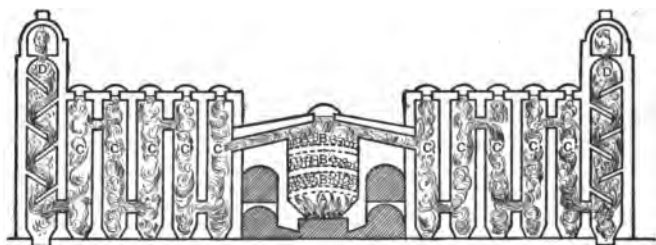
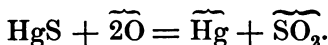


FIG. 174.

nected with a series of condensing chambers, *C, C*, on the sides of which the mercury sublimes.



To separate small quantities of other metals, the Hg is poured into H_2SO_4 or dilute HNO_3 , which dissolves the impurities. It is then distilled and pressed through chamois skin.

Exp. 333. — Heat in an ignition tube a small quantity of dry HgS. Note the SO_2 odor, and any sublimate.

547. Properties. — *Physical.* Mercury boils at about 360° , and freezes at about -40° . It vaporizes, in minute quantities at all temperatures, as can be shown by suspending gold leaf above the liquid. Hg rises and amalgamates with the Au. Mercury is a white liquid of

metallic lustre. When poured upon a plate or glass vessel, it forms in round drops which do not adhere to the vessel. Though the metal may not be poisonous, it is transformed by the fluids of the body into compounds that are. All soluble salts of the element are virulent poisons, about three grains being a lethal dose. The antidote is white of egg. A solution of HgCl_2 is used as an antiseptic in surgery by reason of its germicidal properties.

Chemical. Heated in air below 400° , mercury forms the oxid, HgO . At 400° this compound slowly begins to dissociate into its elements. Mercury forms two classes of salts, the mercurous and mercuric. In the former (*e.g.*, HgCl , HgNO_3) the valence of the metal is 1; in the latter, as HgCl_2 or $\text{Hg}(\text{NO}_3)_2$, it is 2. These two classes of salts differ considerably. HgCl , calomel, is insoluble, and hence nearly non-poisonous, HgCl_2 , corrosive sublimate, is soluble and very poisonous. Hg is not soluble in HCl , but is in *aqua regia*, with formation of HgCl_2 . HgCl can be made by heating Hg with HgCl_2 . It can also be made by precipitation from HgNO_3 solution by HCl or NaCl . HgCl_2 can be made by heating NaCl and HgSO_4 . Changing HgCl to HgCl_2 is oxidation, and the process requires an oxidizing agent. *Aqua regia* is such an agent. Changing HgCl_2 to HgCl is reduction, and it needs a reducing agent, *e.g.*, SnCl_2 . The nitrates of mercury show well the two classes of compounds. Mercury dissolves in HNO_3 . If the acid is cold and dilute and the metal is in excess, the lower nitrate, HgNO_3 , will form. If the acid is hot, concentrated, and in excess, mercuric nitrate, $\text{Hg}(\text{NO}_3)_2$, is the product.

Exp. 334. — Put a little Hg into an evaporating dish, and cover it with dilute HNO_3 . Let it stand 24 hours, and test a little of the liquid with HCl. A white precipitate is HgCl . To some of it add SnCl_2 solution.

Exp. 335. — To a little Hg add quite a quantity of hot, strong HNO_3 , and continue to heat it for some time. Test some of the liquid with HCl, also add SnCl_2 solution.

548. Tests and Separations. — (1) Compounds of mercury fused with dry Na_2CO_3 in an ignition tube give a sublimate of Hg. (2) Zinc or copper in a solution of mercury compounds precipitates mercury, and forms an amalgam of the zinc or copper, a part of which takes the place of the mercury in solution, as $\text{HgCl}_2 + \text{Zn} = \text{ZnCl}_2 + \text{Hg}$. The Hg can afterwards be sublimed in an ignition tube. (3) Mercurous compounds are thrown down, as HgCl , from solution, together with those of silver and lead, by HCl. After removing Pb with boiling water and Ag with ammonia, if Hg' is present, white HgCl is changed by NH_4OH to black $\text{NH}_2\text{Hg}_2\text{Cl}$, amido-mercurous chlorid. The latter can be dissolved in *aqua regia*, as HgCl_2 , and precipitated with SnCl_2 solution, as white HgCl or gray Hg. (4) Mercuric compounds are precipitated, as HgS , with Bi_2S_3 , CdS , CuS , by H_2S , but the Hg precipitate is insoluble in dilute HNO_3 , whereas the other sulfids are soluble. After dissolving the others, the residual HgS is dissolved in *aqua regia*, as HgCl_2 , and tested with SnCl_2 solution. Write the equation for each step in the above. Explain the action of SnCl_2 .

Exp. 336. — Try to dissolve some Hg in HCl. Also in warm *aqua regia*. Test each of the liquids with HCl, and with SnCl_2 solution. Try to dissolve HgCl in *aqua regia*, and test the product.

Exp. 337. — Pour a drop or two of Hg into an evaporating dish, and stir it rapidly with a stirring rod, noting the fine drops. Measure accurately 2 or 3^{cc} of Hg in a graduate, and weigh it. Knowing the weight of H_2O , compute the specific gravity of Hg. Heat one small drop of Hg in an ignition tube. Look for a sublimate, examine it with a lens, and scratch it with a glass rod.

Exp. 338. — Lay a smooth piece of tin foil on a perfectly flat surface. Wash the foil with HCl and dry it. Spread evenly over it a very little Hg. Wash in alcohol a piece of glass the size of the foil. Lay the glass on the foil, weight it, and leave the two pressed together for several days.

Exp. 339. — Place a very little HgCl in a small test tube, and in another HgCl_2 . Heat and volatilize each, noting which liquefies.

Exp. 340. — Make a mixture of a very little HgCl_2 or HgCl , with an equal amount of dry Na_2CO_3 , and heat it in an ignition tube. Look for a sublimate, and determine its character.

Exp. 341. — Dip a piece of bright copper wire into a solution of HgCl_2 , and leave a few moments. Remove, and rub the wire with a cloth. Explain.

Exp. 342. — Try the action on powdered HgCl and HgCl_2 separately of these: NaOH solution, NH_4OH .

Exp. 343. — Add H_2S gas to a solution of HgCl_2 , and note the successive colors of the precipitate — white, yellow, red, brown, black. The first colors are due to double compounds of HgCl_2 and HgS .

549. Uses. — Mercury has a variety of uses, a few of which are: for extracting gold and silver from earthy admixtures, for barometers, thermometers, silvering mirrors, making many amalgams, such as zinc for batteries, cadmium and others for dentists. Its compounds are employed in medicine, surgery, the chemical laboratory, etc.

GOLD.

550. Gold is a heavy, yellow metal, rarely found combined. It has small affinity for other elements, though forming alloys with Cu , Ag , and Hg . Its source is usually either auriferous quartz or sand. In the latter case the deposits are called placer mines. The element is widely distributed, occurring in minute quantities in sea water, soils, etc. Australia and California are the the two greatest gold-producing countries. Gold-bearing quartz is pulverized and treated with Hg to dissolve the yellow metal, which is then separated by distilling off the mercury, and leaving the gold. The malleability of the metal is so great that it has been hammered into sheets less than the twelve-millionth of an inch thick. It does not oxidize, but moist H_2S tarnishes it. On account of its softness, it is usually alloyed with Cu , sometimes with Ag . Pure gold is 24 carats fine, but this is too soft for use, 18-carat gold being as pure as is practicable for most uses. Gold coin, used as the standard of precious metals in most countries, has usually 9 parts Au to 1 part Cu . For plating, jewelry,

alloys with Cu of all grades of fineness, and for a circulating medium, its use is very extensive. The principal compound of gold is AuCl_3 , obtained by dissolving the metal in *aqua regia*, as the common acids do not act on it.

PLATINUM.

551. Platinum is a white metal, much rarer than gold, and is about two-thirds as costly as the latter. Often it is found accompanied with rare elements, like Ir and Os, but not combined with them, as it occurs free or in alloys. Practically it all comes from platinum-bearing sands in the Ural mountains. The sands are from 3 to 7 feet deep, and were discovered in 1819. Pt is one of the heaviest of metals, having 3 times the specific gravity of iron, or $21\frac{1}{2}$ times that of water. It fuses in the oxy-hydrogen flame. Like gold, it has little affinity for other elements, but alloys with many metals. Its tenacity is so great that it can be drawn into wire invisible to the naked eye. This is done in the inside of a silver wire, which is then dissolved away from the Pt by HNO_3 . It is also malleable. The common acids do not dissolve Pt. *Aqua regia* dissolves it, forming H_2PtCl_6 . NaOH , NaNO_3 , etc., act upon it, hence vessels of silver are employed in the treatment of alkalis. Spongy platinum is made by heating PtCl_4 and reducing it to the metal. It has the property of occluding oxygen, which it may in turn impart to other substances, thus acting indirectly as an oxidizer. Platinum is used for sulfuric acid stills, for crucibles, foil, and wire in the chemist's laboratory, and also in electrical work. H_2PtCl_6 is a laboratory reagent. The soluble salts of the metal are precipitated by H_2S .

Exp. 344. — Dissolve a small piece of Pt foil in *aqua regia*, evaporate most of the liquid, add H_2O , and then H_2S gas.

Exp. 345. — Dissolve some gold leaf in *aqua regia*, evaporate the free acid, dilute, and add H_2S .

CHAPTER XL.

SOME ORGANIC COMPOUNDS.

552. Organic Chemistry. — As inorganic chemistry is the chemistry of minerals, or unorganized bodies, so organic chemistry was formerly defined as the chemistry of compounds produced by animals and plants; but since so many of these are now made by the chemist, it is called the chemistry of the carbon compounds. Any compound containing carbon may, therefore, be called an organic compound. In many of these, such as the hydrocarbons and their derivatives, carbon is a central element to which other elements or radicals attach themselves. The molecule of organic matter is often very complex, sometimes containing hundreds of atoms. Chemical affinity is the force which holds together atoms of organic, as well as of inorganic compounds; but for a long time it was supposed that compounds produced by plants or animals had some peculiar *vital force* in addition to that, which made it impossible to synthesize them in the laboratory, though many of them had been analyzed. But in 1828 the barrier between organic and inorganic substances was broken down by Wöhler's making an organic compound, urea, in the laboratory. A short time afterwards a few others were made, and since then tens of thousands of them have been synthesized. Very many are made which have no known existence, except as artificial products. Some

have been predicted to exist, from a theoretical molecular structure, then made, and afterwards found to exist in nature. Artificial organic compounds are far more numerous than inorganic. In addition to qualitative and to quantitative analysis, which give the kind and the quantity of elements in a compound, and from which the empirical symbol of the substance is obtained, the attention of organic chemists has been specially directed since 1860 to structural analysis, which shows the supposed relation or arrangement of atoms in the molecule. Two organic compounds may have the same number of the same kinds of atoms in the molecule and yet have very different properties. The molecular structure of the two substances is quite different. (See Chap. X.) There are now five known compounds having the symbol C_6H_{14} . There are said to be 799 possible compounds having the symbol $C_{13}H_{28}$, only a very small number of which are known.

A great many organic compounds are now made from coal tar, a product of the destructive distillation of soft coal. These compounds include hundreds of rich coloring materials, such as anilin dyes, etc., and of delicate perfumes. Saccharin, a compound several hundred times sweeter than sugar, is one of them. The artificial pigments and dyes have replaced a very large share of the natural ones, such as were once obtained directly from minerals, plants, and animals.

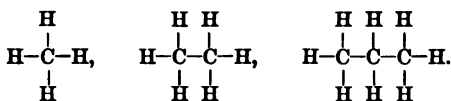
553. Hydrocarbons. — Carbon has usually a valence of 4, and for this reason a vast number of compounds of the element are possible. Any compound of only carbon and hydrogen is called a *hydrocarbon*. Several hundred

such are known to exist, and thousands of others are possible. These are divided into series, each of which has a number of representatives whose composition varies by a regular progression. The most common and abundant of them is the *marsh gas* series (the paraffins), the first member of which is marsh gas, CH_4 . The second member is C_2H_6 , the third C_3H_8 . Each member is derived from the previous by adding CH_2 . The general formula for this series is $\text{C}_n\text{H}_{2n+2}$. There is a second series, the first member of which is C_2H_4 , the second C_3H_6 , the third C_4H_8 , and the general formula C_nH_{2n} . This is called the *olefiant* series, the members of which are *olefines*. A third series has the first members, C_2H_2 (acetylene), C_3H_4 , etc., and the general formula $\text{C}_n\text{H}_{2n-2}$. The members of this series are called the *acetylene hydrocarbons*. Other series have $\text{C}_n\text{H}_{2n-4}$, $\text{C}_n\text{H}_{2n-6}$, etc. The first and fifth groups are by far the most important, their representatives and derivatives the most numerous and valuable. To the paraffins belong the various substances derived from petroleum, such as naphtha, kerosene, paraffin. Also among the paraffin derivatives are the various commercial alcohols, and series of ethers, acids, etc. $\text{C}_n\text{H}_{2n-6}$, the benzene or aromatic series, is a very large and interesting group. It is the basis of the anilin dyes, and of many perfumes and flavors. The first of this series is benzene, C_6H_6 . The list of series runs much higher, one having been found with $\text{C}_{50}\text{H}_{46}$, belonging to $\text{C}_n\text{H}_{2n-54}$. Theoretically the list may continue without limit.

554. The Paraffins.—The first ten of the paraffins are named and symbolized as follows:

SYMBOLS.	NAMES.	EQUIVALENTS.	NAMES.	BOILING-POINTS.
1. CH ₄	methane	CH ₃ H	methyl hydrid	gas.
2. C ₂ H ₆	ethane	C ₂ H ₅ H	ethyl "	"
3. C ₃ H ₈	propane	C ₃ H ₇ H	propyl "	"
4. C ₄ H ₁₀	butane	C ₄ H ₉ H	butyl "	1°
5. C ₅ H ₁₂	pentane	C ₅ H ₁₁ H	pentyl "	38°
6. C ₆ H ₁₄	hexane	C ₆ H ₁₃ H	hexyl "	69°
7. C ₇ H ₁₆	heptane	C ₇ H ₁₅ H	heptyl "	100°
8. C ₈ H ₁₈	octane	C ₈ H ₁₇ H	octyl "	125°
9. C ₉ H ₂₀	nonane	C ₉ H ₁₉ H	nonyl "	149°
10. C ₁₀ H ₂₂	dekane	C ₁₀ H ₂₁ H	dekyl "	173°

This series extends as far as C₃₅H₇₂. Crude petroleum, which issues from the earth, contains these hydrocarbons as high as 30. The different ones are separated by fractional distillation—as they boil at different temperatures—and by subsequent treatment with H₂SO₄, etc. The first few are gases at usual temperatures. CH₄ is a light hydrocarbon, having a vapor density of only 8, whereas C₄H₁₀ is a comparatively heavy one, with vapor density 29. From 5 to 15 in the series the compounds are liquid, and below 15 are solid, the lightest being crystalline; 6 and 7 are mostly gasoline, benzine (not benzene) is mostly 7, naphtha 7 and 8, kerosene 9 and upwards. Explosions of kerosene are caused by the presence of the lighter hydrocarbons, as naphtha. Structurally the first three of the series are:

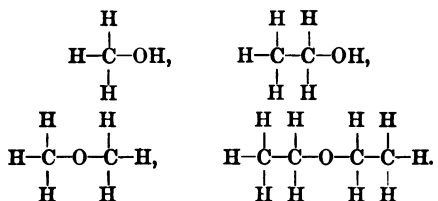


555. The Alcohols and Ethers.—The so-called *ethereal radicals* in the above series are CH₃, C₂H₅, C₃H₇, etc., each with a valence of one. The paraffins are hydrids of these radicals. Instead of the radicals combining with H to form paraffins, they may unite with OH, in which case they form *hydroxids* or *alcohols*; they may also be made to unite with oxygen, and then they form a series of *oxids* or *ethers*. The first three of these are:

1. CH₃OH methyl hydroxid, or methyl alcohol.
2. C₂H₅OH ethyl " " ethyl "
3. C₃H₇OH propyl " " propyl "

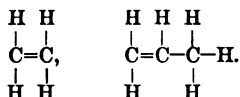
1. $(\text{CH}_3)_2\text{O}$ methyl oxid, or methyl ether.
2. $(\text{C}_2\text{H}_5)_2\text{O}$ ethyl " " ethyl "
3. $(\text{C}_3\text{H}_7)_2\text{O}$ propyl " " propyl "

These alcohols and ethers may be derived from the paraffins by replacing a portion of the hydrogen with OH or O. Commercial alcohol is 2, or ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$; wood spirit is mainly 1. The ether of commerce (sulfuric ether) is 2, *i.e.*, $(\text{C}_2\text{H}_5)_2\text{O}$. Structurally the first two symbols are:



The number of substitutions of different elements and radicals for the successive hydrogen atoms in these series is almost unlimited. By substituting Cl for 1H in CH_4 , we have CH_3Cl ; 2Cl for 2H, CH_2Cl_2 ; 3Cl for 3H, CHCl_3 ; replacing 4H with 4Cl, CCl_4 . CHCl_3 is the common anæsthetic chloroform; CHBr_3 is bromoform; CHI_3 iodoform. Not only elements but radicals can be substituted for successive hydrogen atoms. Anilin, $\text{C}_6\text{H}_5\text{NH}_2$, first made from indigo in 1826, can be prepared by substituting NH_2 for H in benzene, C_6H_6 . The first anilin dye was made in 1856 from $\text{K}_2\text{Cr}_2\text{O}_7$ and anilin sulfate.

556. Olefins.—The second series of hydrocarbons, represented by C_nH_{2n} , begins with C_2H_4 , olefant gas, the second and third being C_3H_6 , C_4H_8 . Structurally the first two olefins are:



557. Marsh Gas.—Methane or marsh gas, CH_4 , is a combustible substance found in marshes where oxygen does not reach decaying organic matter. It issues from the coal and causes most explosions in coal mines, the

products of its combustion or explosion being CO_2 and H_2O . Miners call it *fire damp*; the product CO_2 , they call *choke damp*. Next to hydrogen it is the main constituent of illuminating gas resulting from the distillation of soft coal, and is present in large amounts in "natural gas." Being one of the lighter hydrocarbons, its combustion gives little light. It can be prepared by heating NaOH with $\text{NaC}_2\text{H}_3\text{O}_2$, $\text{NaOH} + \text{NaC}_2\text{H}_3\text{O}_2 = \text{Na}_2\text{CO}_3 + \widetilde{\text{CH}_4}$, *i.e.*, by the action of a base on an acetate.

558. Acetylene. — This, C_2H_2 , is one of the most interesting of the hydrocarbons, being a gas which burns with a dazzling white light, and which may sometime supplant ordinary gas as a luminant. It is now made in quantity from calcium carbide, CaC_2 , by the action of the latter on water. $\text{CaC}_2 + 2\text{H}_2\text{O} = \text{Ca}(\text{OH})_2 + \widetilde{\text{C}_2\text{H}_2}$. CaC_2 can be made by heating lime and carbon. $\text{CaO} + 3\text{C} = \text{CaC}_2 + \widetilde{\text{CO}}$. Small quantities of acetylene are formed in the inner cone of the gas and candle flames, and to it in part is thought to be due the illuminating power of those flames.

559. Exothermic and Endothermic Reactions. — In the formation of a majority of compounds heat is liberated, but there are some which, in their formation, absorb heat. To the latter class belongs C_2H_2 . Reactions which liberate heat are known as *exothermic*, those which absorb heat and cool surrounding space are called *endothermic*. Substances formed from endothermic reactions usually are unstable, as HI , and easily break up.

Exp. 346. — Throw a small piece of CaC_2 into a tumbler of water, and ignite the escaping gas. Take a piece of CaC_2 in some iron tongs, sprinkle it with some H_2O from a wash bottle, set the gas on fire, and try to extinguish the flame with a fine spray of water.

560. Illuminating Gas. — This is usually made by one of two methods, either from water and carbon — the product of which gives water gas, described in Chap. XXI — or by the destructive distillation of bituminous coal. In the latter case retorts of iron or fire clay are filled with soft coal and heated to 1100° or more, over a coal fire (Fig. 175). From the retorts tubes lead upward into a

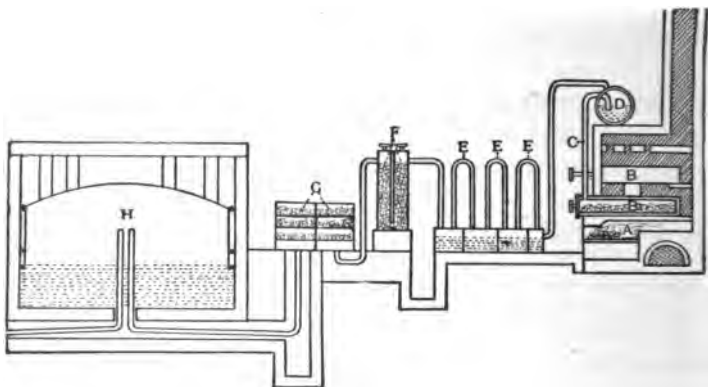


FIG. 175. — Gas plant. *A*, furnace in which fire is kept for heating *B*, retorts; *C*, conductor to *D*, hydraulic main; *E*, condensers; *F*, washers; *G*, purifiers; *H*, gas-holder.

large pipe called the *hydraulic main*, through which water is kept flowing. As the coal is heated, the gaseous products of the distillation, together with some of the liquid, semi-liquid, and solid products, — such as coal tar, ammonium compounds, sulfur, carbon dioxid, — pass into the water of the hydraulic main, and are there washed and in part deposited. The insoluble gases pass on through several hundred feet of vertical pipes, called the *condensers*, beneath which there is water to remove more of the impurities. The gas then goes into towers known as

washers or *scrubbers*, and is met by a falling spray of water, which washes out soluble gases, like H_2S , NH_3 , etc., and remaining traces of solids. It then goes, for final purification, into chambers containing lime, CaO , or hydrated ferric oxid, which are called *purifiers*. Finally the gas, having been made sufficiently pure for use, is conducted into a circular chamber known as the *gas-holder*, and is thence distributed to consumers. Coke is the solid residue left in the retorts. Some gas carbon is also found here. Coal tar, from which so many organic compounds are now made, and ammonium compounds, the source of most commercial ammonia, are obtained from the hydraulic main and the condensers.

561. Composition. — Even when freed from its impurities, coal gas is a very complex mixture. The constituents may be divided into three classes, *luminants*, *diluents*, and *impurities*. The luminants, or light-giving portions, consisting of hydrocarbons that are rich in carbon, as C_2H_2 , C_6H_6 , C_2H_4 , do not constitute more than 4 to 6% of the gas; in fact, much less than that until the gas has been enriched by the destructive distillation of either cannel coal, naphtha, or petroleum. These give the above hydrocarbons, a small per cent of which is mixed with the gas. Impurities, such as CO_2 and nitrogen, make up 3 to 5% more of the gas. In larger quantities they would impair the efficiency of the flame. Ninety per cent or more of the gas is composed of diluents, which are combustible, but give only little light. These diluents exist in gas about as follows: H 45%, CH_4 40%, CO 5%.

Much of the gas now consumed in large cities is water gas. It differs in composition from that described above

in containing 5 or 6 times as much CO, the percentage being from 25 to 30. The amount of gas used for lighting purposes is something enormous. Boston consumes some 2,500,000,000 cubic feet annually.

562. Natural Gas comes from the earth in certain places, as in Pennsylvania and Ohio, in vast quantities. It consists of CH_4 and other hydrocarbons, and appears to have had an origin similar to that of petroleum and coal, in that it represents preëxisting vegetable life. The reservoirs of natural gas very often occur in sandstone, usually in the vicinity of coal beds. The gas may be a product of the destructive distillation of coal in the earth's interior.

Exp. 347. — Put into an ignition tube some pieces of cannel coal, attach a delivery tube, and connect with a pneumatic trough. Heat the contents of the tube, and collect the escaping gas like oxygen. After heating some time, examine the tube for solid and semi-liquid substances, and test the combustibility of the gas.

563. Alcohol. — The most important of alcohols are methyl, CH_3OH , and ethyl, $\text{C}_2\text{H}_5\text{OH}$. The former is called wood spirit, is obtained in an impure state by distilling wood, and is used to dissolve resins, fats, oils, etc., and in making anilin.

Ethyl alcohol, or spirit of wine, is commercial alcohol. It is prepared by fermenting glucose, and distilling the product. As it boils at 78° , it can be separated from the water, etc., with which it is mixed, by fractional distillation, *i.e.*, distilling only a portion of the liquid. The alcohol will first pass over. By successive fractional distillations, 94 or 95% alcohol can be obtained. This is the best commercial article, though most grades fall far below it. The remainder of the water can be taken out by distilling it with CaO or BaO . One hundred per cent constitutes absolute alcohol, which is a deadly poison. When

diluted it increases the circulation, stimulates the system, hardens the tissues by withdrawing water, and is the intoxicating principle in all liquors. It readily evaporates, and is very inflammable, giving little light, but much heat.

Beer has usually from 3 to 6% alcohol, wines from 8 to 20%. In Massachusetts, liquors containing 1% alcohol are regarded as intoxicating; in many states 3% is the limit by law.

Exp. 348. — Introduce 20^{cc} of molasses into a flask of 200^{cc}, fill it with water to the neck, and put in half a cake of yeast. Fit to this a delivery tube, and pass the end of it into a test tube holding a clear solution of lime water. Leave in a warm place for two or three days. Then look for a turbidity in the lime water, and account for it. See whether the liquid in the flask is sweet. The sugar should be changed to alcohol and CO₂. This is fermented liquor; it contains a small percentage of alcohol.

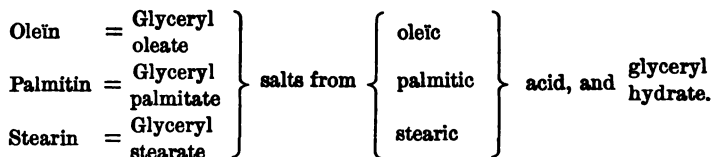
Exp. 349. — Attach the flask used in the last experiment to the apparatus for distilling water, and distil not more than one-fifth of the liquid, leaving the rest in the flask. The greater part of the alcohol will pass over. To obtain it all, at least half of the liquid must be distilled; what passes over towards the last is mostly water. Taste and smell the distillate. Put some into an evaporating dish and touch a lighted match to it. If it does not burn, redistil half of the distillate and try to ignite the product. Try the combustibility of commercial alcohol; of Jamaica ginger, or of any other liquid known to contain alcohol.

Exp. 350. — Put a little of the white of egg into an evaporating dish or a beaker; cover it with strong alcohol and note the effect. Strong alcohol has the same coagulating action on the brain and on the tissues generally, when taken into the system, absorbing water from them, hardening them, and contracting them in bulk.

Exp. 351. — To show the contraction in mixing alcohol and water, measure exactly 5^{cc} of alcohol and 5^{cc} of water. Pour them together, and presently measure the mixture. The volume is diminished. A strip of parchment soaked in water till it is limp, then dipped into strong alcohol, becomes again stiff, owing to the attraction of alcohol for water.

564. Oils and Fats.—Oils and fats are insoluble in water; the former are liquid, the latter are solid. Most fats are obtained from animals, oils from both plants and animals. Oils are classified as *fixed* and *essential*. Castor oil is an example of the former and oil of cloves of the latter. Fixed oils include *drying* and *non-drying* oils. They leave a stain on paper, while essential, or volatile, oils leave no trace, but evaporate readily. Essential oils dissolved in alcohol furnish essences. They are obtained by distilling with water the leaves, petals, etc., of plants. Drying oils, as linseed, absorb O from the air, and thus solidify. Non-drying ones, as olive, do not solidify, but develop acids and become rancid after some time.

Oils and fats are salts of fatty acids and the base glycerin. The three most common of these salts are olein, found in olive oil; palmitin, in palm oil and human fat; and stearin, in lard. The first is liquid, the second semi-solid, the last solid. Most fats are mixtures of these and other salts.



565. Soaps, etc.—Saponification consists in separating fats or oils into the base glycerin, and the respective acid or salt. When glycerin is the main product it is prepared by passing over the fat superheated steam under pressure. Glycerin, or glyceryl hydroxid, is a sweet, thick, colorless, unctuous liquid, used in cosmetics, unguents, pomades, etc., and has the symbol $\text{C}_3\text{H}_5(\text{OH})_3$. From it

is made nitroglycerin. Soap-making illustrates a species of saponification. In this the fat or oil is acted on by the hydroxid of sodium, if a hard soap is desired, or by potassium hydroxid, if a soft soap. For the reaction see p. 143.

Soaps are thus salts of fatty acids and the hydroxid of sodium or potassium, and are soluble in soft water. The grease which exudes from the skin or appears in fabrics to be washed, is attacked by the sodium stearate and converted into an emulsion, then, together with the suspended dirt, is removed.

If hard water contains dissolved salts of Ca, these salts at once react with sodium stearate, etc., and form insoluble stearate of Ca, *i.e.*, a lime soap. Hence in hard water soap will not dissolve or cleanse, till all the Ca or Mg salts have combined.

566. Nitroglycerin, etc.—Treated with nitric acid, glycerin forms the very explosive and poisonous liquid, nitroglycerin. $C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(NO_3)_3 + 3H_2O$. Sulfuric acid is used in the process to absorb the water formed. For obvious reasons beginners should not experiment with these substances. Nitroglycerin absorbed in some substance like sawdust, gunpowder, or diatomaceous earth, forms dynamite.

Gun-cotton is made by "nitrating" cotton fiber or cellulose, *i.e.*, treating it with HNO_3 , H_2SO_4 being used as before to absorb H_2O . Although the fiber appears unchanged, it has by the process been converted into a dangerously explosive compound, which leaves no ash on burning.

CHAPTER XLI.

CHEMISTRY OF FERMENTATION AND OF LIFE

OF FERMENTATION.

567. Ferments.—A large number of chemical changes are brought about through the direct agency of bodies called ferments, their action being known as fermentation. In most cases these bodies are microscopic, single-celled plants, known variously as *germs*, *microbes*, *microörganisms*, *bacteria*, *bacilli*, etc. They feed upon the substance, meanwhile multiplying with great rapidity, and transform it into other compounds. Pasteur was a pioneer in the

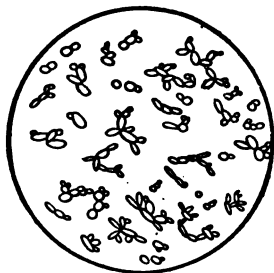


FIG. 176. —Yeast much magnified.

study of microbes, and he has been called the “founder of bacteriology.” His work was begun about 1860, since which time all the information of the causes of fermentation and of infectious diseases has been accumulated. The temperature best suited to the rapid multiplication of germs is 25° to 35° . They are usually killed at about the boiling-point of water, or at the freezing-point. They may become dormant in dry air or soil, but are resuscitated on being put into water, or a suitable “culture medium.” Yeast (Fig. 176) is one of the most common of these ferments. It is a microscopic plant

found on the ground near apple trees and grape vines, and often in the air. The cultivated variety sold by grocers is often grown in the starch of potato, and is then called potato yeast.

568. Fermentation. — Like other ferments, yeast grows and multiplies very rapidly. A cell divides into several parts, and each part becomes a separate cell. These new cells divide in a like manner, and so on, and thus in a few days an enormous number of yeast plants are produced. The food on which yeast thrives best is a dilute solution of a sugar called glucose, $C_6H_{12}O_6$. This is found in the juices of most fruits. When yeast germs come in contact with the juice of the grape, apple, etc., fermentation sets in, the sugar is changed by the yeast into alcohol, and carbon dioxid is liberated. Some other substances are formed, but the main reaction which ensues is: $C_6H_{12}O_6 = 2C_2H_6O + \overline{2CO_2}$. Several days or weeks may be necessary for the completion of the process, but eventually all the sugar is changed to alcohol and CO_2 . If the fermentation takes place in the juice of apples, the product, containing a small per cent of alcohol, is known as cider. The fermented juice of other fruits, like grapes, is called wine. Each of these liquids contains a dilute solution of alcohol, which, on distillation, forms strong alcohol. The action of yeast in bread-raising is the same kind of fermentation as that described above. The CO_2 and alcohol formed cause the dough to rise, and make the bread porous.

There exist a great number and variety of ferment plants. Each species seems to prefer a different sort of

food, and the products of fermentation are also very different. There are germs which feed upon alcohol, in the dilute form. Such a ferment in the cider mentioned above changes the alcohol to acetic acid, and the cider then becomes vinegar, which contains not over 5% of the acid. In that case it is known as acetic fermentation, and the ferment is quite different from yeast, the reaction being $C_2H_6O + 2\widetilde{O} = HC_2H_3O_2 + H_2O$. "Mother of vinegar" consists of the acetic ferment. The acetic acid itself may undergo still another fermenting process by a different microörganism, lose all its acid properties, and be changed to water and CO_2 . $HC_2H_3O_2 + 4\widetilde{O} = 2H_2O + \underbrace{2CO_2}$.

Lactic fermentation changes the sugar of milk, lactose, to lactic acid, and the milk becomes sour. Most spontaneous changes in organic substances are due to microörganisms. The finest kind of butter is now made by the introduction into the cream of a special microbe. Nitrates and nitrites are prepared by the action of germs on waste organic matter. The germ seems to have power to take inert nitrogen from the air, and unite it into compounds.

Putrefaction is a fermentation in which the products of decay are ill-smelling. The organisms—called *saprophites* when they feed on dead matter—cause the matter to putrefy. This action, as well as that of ordinary fermentation, used to be attributed solely to oxygen. Oxygen very often aids and hastens the action of ferments, but is not the chief agency.

569. Infectious Diseases are known to be caused by bacteria of different kinds (Fig. 177). These germs obtain a foothold in the tissues of the human body through food or drink or dust particles in impure air which may be laden with them, or through the act of kissing a person having the disease. All infectious diseases are now regarded as

germ diseases. Such are smallpox, typhoid fever, scarlet fever, diphtheria, measles, tuberculosis, and a host of others. Milk or water containing any of these germs, meat of tuberculous or otherwise diseased animals, taken into the stomach is very likely to transfer the bacteria and give the person that disease. Some of these germs are very virulent, and multiply so fast that from a single one no less than 300,000,000,000 may be produced in 48 hours. In some diseases 15,000,000,000 are estimated to exist in a cubic inch of flesh. The germs do not spring into life spontaneously from inorganic matter, but always come from pre-existing similar forms.

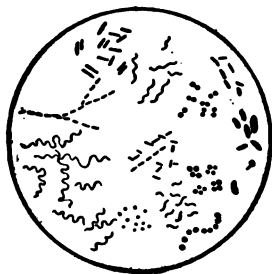


FIG. 177. — Bacteria of different sorts, which give rise to various infectious diseases, very much magnified.

A person suffering from tubercular consumption may in expectorating throw out millions of these bacteria, which dry up and are taken into the lungs with dust particles from the air. They may obtain a foothold in the lungs, or they may not if the system is strong enough to overcome them. The best safeguard is a healthy physical condition, not weakened by bad habits or violation of the laws of health. Here we find a most potent argument against intemperance in drinking, in eating, or in exercise, and against every vicious practice and excess of any sort which depresses the system; for the enfeebled body becomes an easy prey to disease.

An antiseptic (also called a disinfectant or germicide) is a substance which destroys the germ, and prevents the disease. Very many germicides kill not only the bacteria but also, unless they are much diluted,

the person himself. Rooms in which cases of infectious diseases have been confined are disinfected by burning sulfur or wood alcohol, etc. Carbolic acid, hydrogen dioxid, superheated steam, etc., are employed in different cases. For dressing wounds in hospitals a weak solution of HgCl_2 is used as a wash.

The philosophy of vaccination — which has been more successful in smallpox than in any other disease — is that a less virulent type of the germ is introduced into the system, and hence the person has a very mild form of the disease, but is rendered immune for a longer or shorter time, and hence does not have the disease even though exposed to it. The germ with which he has been vaccinated has been weakened by domestication. This may be accomplished in two ways: (1) by introducing the virus into an animal (as a cow) that is not strongly affected by it, then transferring the new virus from the cow to the arm of the man; (2) by growing several generations in a prepared liquid, or culture medium. If several watch-glasses be arranged, each containing some of a liquid suitable for the growth of the germ, and a single drop of an infected liquid be put into the first glass, this liquid will soon teem with a second generation of germs, a drop of which is then put into the second glass. After a time the third liquid is inoculated, and so on. Each crop becomes less virulent than the previous. With the virus of one of these cultures the person is vaccinated.

OF LIFE.

570. Growth. — The chemistry of organic life is very complex, and not well understood. A few of the principal points of distinction between the two great classes of living organisms, plants and animals, are all that can be noted here. Minerals grow by accretion, i.e., by the external addition of molecules of the same material as their interior. A crystal of quartz grows by the addition of successive molecules of SiO_2 , arranged in a symmetrical manner around its axis. The growth of crystals can be seen by suspending a string in a supersaturated solution of CuSO_4 or of sugar. In plants and animals the growth is very much more complex, but is from the interior, and is

produced by the multiplication of cells. To produce this cell growth and multiplication, food materials must be furnished and assimilated. In plants, sap serves to carry the food materials to the parts where they are needed. In the higher animals, various fluids, the most important of which is the blood, serve the same purpose.

571. Chemistry of Plants. — In ultimate analysis, plants consist mainly of C, H, O, N, P, K. In proximate analysis, as it is called, they are found to contain these elements combined to form substances like starch, sugar, etc. Water is the leading compound in both animals and plants. One of the most important differences between animals and plants is, that all plants, ex-



FIG. 178. — Potato starch much magnified.

cept parasitic ones, are capable of building up such compounds as starch (Figs. 178, 179) from mineral food-stuffs, while animals have not that power, but must have the products of proximate analysis ready prepared, as it were, by the plant. Hence plants thrive on minerals, whereas animals feed on plants or on other animals. The power which plants have of transforming mineral matter is largely due to sunlight, the action of which in separating CO_2 was described on page 82. The reaction in the synthesis of starch from CO_2 and H_2O in

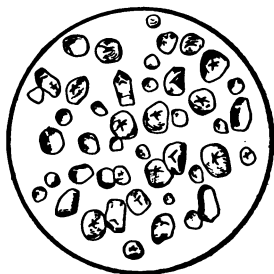


FIG. 179. — Corn starch much magnified.

the leaf, is thought to be as follows : $6\text{CO}_2 + 5\text{H}_2\text{O} = \text{C}_6\text{H}_{10}\text{O}_5 + 12\text{O}$. $\text{C}_6\text{H}_{10}\text{O}_5$ is taken into the tree as starch ; 12O is given back to the air. All the constituents, except CO_2 and a very small quantity of H_2Q , are absorbed by the roots, from the soil, from which they are soon withdrawn by vegetation. To renew the supply, fertilizers or manures are applied to the soil. These must contain compounds of N, P, and K. N is usually applied in the form of ammonium compounds, *e.g.*, $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{CO}_3$, and NH_4NO_3 . The reduction and application of $\text{Ca}_3(\text{PO}_4)_2$ for this purpose was described on page 123. K is usually applied in the form of KCl and K_2SO_4 .

572. Food of Man.—In the higher animals the object is not so much to increase the size as to supply the waste of the system. The principal elements in man's body are C, H, O, N, S, P.

An illustration of the transformation of mineral foods by plants before they can be used by animals is found in the $\text{Ca}_3(\text{PO}_4)_2$ of bones. This is rendered soluble ; plants absorb and transform it ; animals eat the plants and obtain the phosphates.

The food of mankind may be divided into four classes : (1) proteids, which contain C, H, O, N, and often S and P ; (2) fats, and (3) amyloids, both of which contain C, H, O ; (4) minerals. Examples of the first class are the gluten of flour, the albumen of the white of egg, and the casein of cheese. To the second class belong fats and oils ; to the third, starch, sugar, and gums ; to the fourth, H_2O , NaCl, and other salts. Since only proteids contain all the requisite elements, they are essential to human food, and are the only absolutely essential foods, except

minerals; but as they do not contain all the elements in the proportion needed by the system, a mixed diet is indispensable. Milk, better than any other single food, supplies the needs of the system. The digestion and assimilation of these food-stuffs and the composition of the various tissues is too complicated to be taken up here; for their discussion the reader is referred to works on physiological chemistry.

573. Conservation.—Plants, in growing, decompose CO_2 , and thereby store up energy, the energy derived from the light and heat of the sun. When they decay, or are burned, or are eaten by animals, exactly the same amount of energy is liberated, or changed from potential to kinetic, and the same amount of CO_2 is restored to the air. The tree that took a hundred years to complete its growth may be burned in an hour or be many years in decaying; but in either case it gives back to its mother Nature, all the matter and energy that it originally borrowed. The ash from burning plants represents the earthy matter, or salts, which the plant assimilated during its growth; the rest is volatile. In the growth and destruction of plants or of animals, both energy and matter have undergone transformation. Animals, in feeding on plants, transform the energy of sunlight into the energy of vitality. Thus “we are children of the sun.”



APPENDIX.

METRIC MEASURES, WEIGHTS, CONVERSION TABLES, TEMPERATURES, Etc.

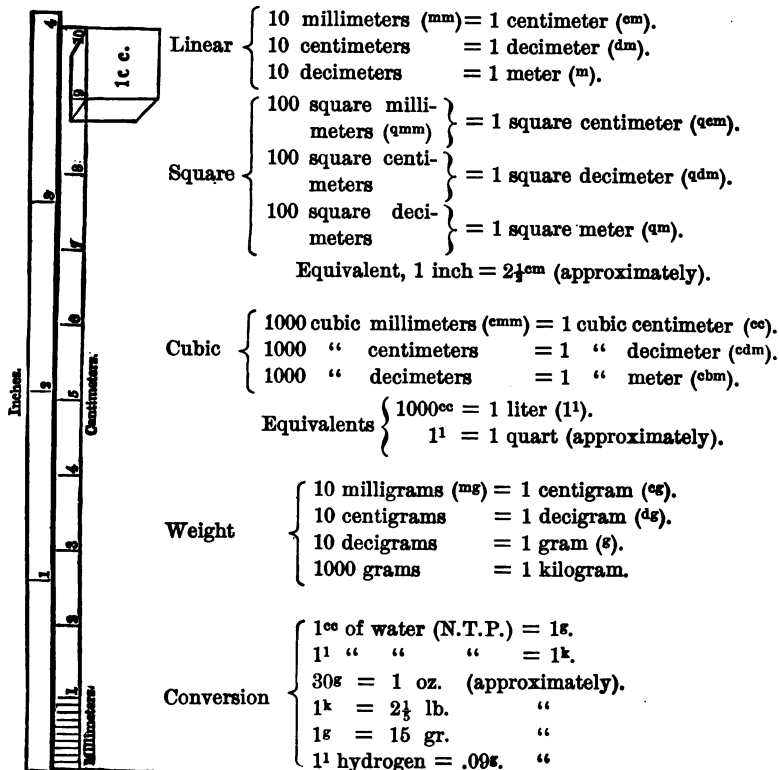


FIG. 180.

The metric system is always employed in chemistry. Unless otherwise mentioned, degrees of heat, as used in this book, are of the centigrade scale, C., in which the freezing-point of water is 0° , and its boiling-point 100° , under 760^{mm} pressure. If Fahrenheit degrees, in which the freezing-point of water is -32° and the boiling-point 212° , are meant, F. is placed after the figures. To convert C. to F., multiply by $\frac{9}{5}$, and add 32° (i.e., $C. \times \frac{9}{5} + 32$). To convert F. to C., subtract 32° , and take $\frac{5}{9}$ of the remainder [i.e., $(F. - 32) \times \frac{5}{9}$]. For the absolute scale, A., see p. 220.

GLASS-WORKING, Etc.

It is obviously impossible to give a full treatise on chemical manipulation in a work of the scope of the present one; nor is it necessary, as most teachers are sufficiently familiar with preparing and setting up chemical apparatus. The brief treatment here given the subject is for the pupil at the outset of his work.

To break Glass Tubing.—Lay the tubing on a flat surface, and draw a sharp three-cornered file two or three times at right angles across it where it is to be broken, till a scratch is made. Take the tube

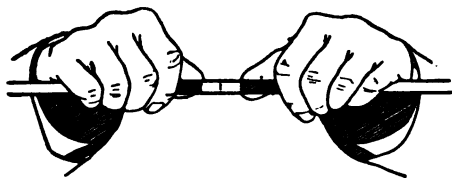


FIG. 181.

in the hands, having the two thumbs nearly opposite the scratch, and the fingers on the other side (Fig. 181). Press outward quickly with the thumbs, and at the same time pull the hands strongly apart, and the

tubing should break squarely at the scratch.

To break large tubing, or cut off bottles, lamp chimneys, etc., first make a scratch as before; then heat the handle of a file, or a blunt iron—in the blast-lamp flame by preference—till it is red hot, and at once press it against the scratch till the glass begins to crack. The fracture can be led in any direction by keeping the iron just in front of it. Re-heat the iron as often as necessary.

To cut Glass.—Lay the glass plate on a flat surface, and draw a steel glass-cutter—revolving wheel—over it, holding this against a ruler for a guide, and pressing down hard enough to scratch the glass. Then break it by holding between the thumb and fingers, having the thumbs

on the side opposite to the scratch, and pressing them outward while bending the ends of the glass inward. The break will follow the scratch.

Holes can be bored through glass and bottles with a broken end of a round file kept wet with a solution of camphor in oil of turpentine.

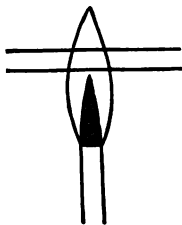


FIG. 182.

To make Ignition Tubes.—Take a piece of wide tubing 20 or 25^{cm} long, hold it *steadily* in the Bunsen flame *just above the inner greenish cone* (Fig. 182) and rotate it. When it begins to soften, draw it out slightly (Fig. 183 A) and raise it a little in the flame. Do not pull or twist the glass, but *let the heat gradually separate it*, so as not to have long threads attached. Do not let the hot end of the glass touch any object till it becomes cool. The

ends may be rounded, B, by holding and rotating them in the edge of the flame. Finally anneal the glass by closing the lower openings of the lamp and holding the heated end in the flame to cover it with soot, then letting it cool gradually *without touching any object*. Unless great care is taken in this cooling, the glass will break when next put into the flame. Save the tubes for subsequent experiments.

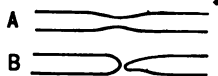


FIG. 183.

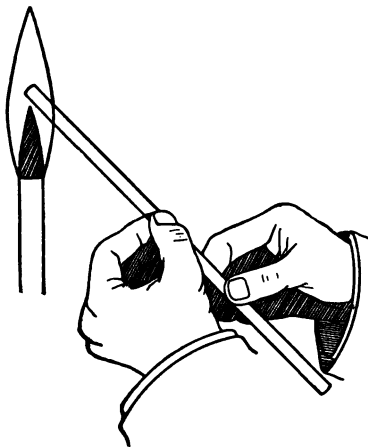


FIG. 184.

To make Stirring Rods.—Weld the ends of a piece of glass tubing about 20^{cm} long and 6^{mm} in diameter by holding each end successively in a Bunsen flame above the green one, (Fig. 184) and rotating it constantly till the openings are sealed. Use care in cooling it, as before.

To bend Glass Tubing.—1. For bending glass use the ordinary gas flame (Fig. 185) or a fish-tail attachment to a Bunsen burner, as the Bunsen flame is too hot.

Turn down the gas till the flame is about 5^{cm} across. Bend in the middle and at right angles each of 2 or 3 pieces of glass tubing 14^{cm} long, as follows: Take the *ends* of the tube lightly in the fingers and hold the *middle lengthwise in the flame, just above the dark part*. It must be kept constantly in the flame and slowly rotated with the fingers. It will soon be covered with soot and finally begin to soften, the part which is near the middle of the flame yielding first. A slight pressure indicates the softening. When it begins to soften take it quickly from the flame and—holding it between the eye and a window sash or other right angle, with one eye closed—bend it at right angles (Fig. 186). If it does not bend easily, heat it again. *Before wiping off the soot let the tube cool in such a position that the hot portion will not touch any object.* Bend the other short tubes in the same way.

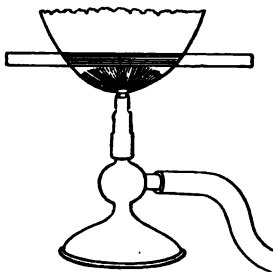


FIG. 185.



FIG. 186. — A correct. B incorrect.

2. Bend at right angles another tube 22 or 24^{cm} long, having the middle of the bend about 6^{cm} from one end (remember that that part of the glass will bend which is in the middle of the flame). Cool this as before. Bend still another tube, 40^{cm} long, 6^{cm} from one end. When the tubes are reasonably cool wipe off the soot with a dry cloth or tissue paper.

3. Round the ends of each tube by holding their tip ends for a minute in a Bunsen flame, and when they are cool test the result with the fingers. For their use, see Exp. 81, p. 112.

To make Delivery Tubes, etc.

— 1. Examine the angles and the relative lengths of the parts of a delivery tube (d.t.) in a model and in Fig. 187. Note that the parts all lie in the same plane or nearly so (close one eye, and sight along the tube 1, a, b, c, 2); that there are three bends, a, b, c, and that the angles are all obtuse; that a and c are near the end of the tube (6 or 8^{cm}); that the bends are made in such a way that when the tube is put into a gas generator (Fig. 188) the end

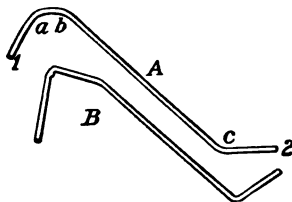


FIG. 187. — A correct. B incorrect.

does not touch the bench, nor is it so high as not easily to go under the shelf of a pneumatic trough. In preparing a delivery tube pupils must bear all these directions in mind, and it is often desirable to practise with old glass tubes, especially noting that all parts lie in the same plane. It is better to make two bends at *a*, *b* rather than one, though the two are close together. Make the bends in the order *a*, *b*, *c*, and as follows:

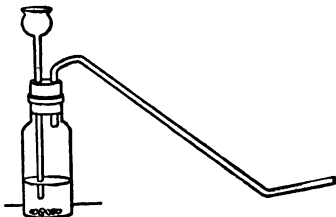


FIG. 188.

2. Use a piece of tubing 50^{cm} long, and holding the short portion 1 *a* in the right hand, heat it as in Fig. 185, in the fish-tail flame. When it softens take it quickly from the flame and sight along the tube with one eye closed as you bend it. Avoid bending it too much. Bend at *b* in the same way, having the bend close to *a*. As you bend it sight along the parts 1, *a*, *b*, 2. Then bend *c*, holding 2 in the right hand. Sight along 2, *c*, *b*, *a*, 1. Cool it cautiously, as before. Round the sharp ends 1, 2 in a Bunsen flame, as previously. Show the result to the instructor.

To perforate Stoppers and adjust Tubes.—1. To a test tube ($5 \times \frac{5}{8}$ or $6 \times \frac{3}{4}$ in.) fit a cork, then remove the latter and with a round file bore a hole through it, holding it in the left hand between the thumb and fingers and pressing the end of the file against the middle of its *larger surface*. *Observe constantly during the operation whether the file is perpendicular to the surface of the cork.* Make a perfectly circular orifice, reversing the cork so as to have it of uniform bore throughout. The hole must be a little smaller than the tube it is to receive. When the operation is completed put the end of the delivery tube (1 *a*, Fig. 187) through the hole, and adjust the stopper to the test tube. Detach the stopper from the test tube, not from the delivery tube.

2. The apparatus described above is for use where there are only solids. If a liquid is employed, a stopper with two openings is needed, one of which is for a thistle tube. For Wolff bottles, a third hole for a safety tube is desirable.

3. Rubber stoppers may be used instead of cork, thus saving much time in preparation. To insert a tube in a rubber stopper, *wet both the tube and the orifice of the stopper*. Tubes should be detached from rubber stoppers when you are through using them. Every tube before insertion in a stopper should have had its end rounded in the edge of the Bunsen flame.

Filtration and Washing. — Circular filter papers (5" in diameter) are folded as in Fig. 189, three folds on one side, and one on the other. Before filtration, the substances in the test tube should be thoroughly shaken (Fig. 190), away from the bench, and the contents

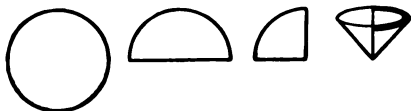


FIG. 189.



FIG. 190.

quickly poured on the filter (Fig. 191), in such a manner as not to spatter it over the top of the paper. The residue on the paper is washed by forcing with the breath a fine spray of water from the pointed end, A, of the tube (the mouth being applied at B, Fig. 192), on the residue,

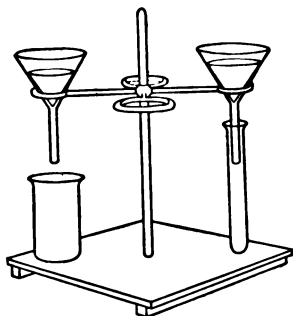


FIG. 191.



FIG. 192.

and letting the water run through the filter into a clean test tube. This carries off any substance that will dissolve in the water.

Test Tubes, Racks, etc. — For ordinary use test tubes should be either 5" \times $\frac{3}{8}$ " or 6" \times $\frac{3}{8}$ ". For gas generators as for oxygen, use 7" \times $\frac{7}{8}$ " tubes. For certain ignition tubes hard glass tubing is used, which can scarcely be worked with the Bunsen flame. Such tubes are better bought than made from tubing.

For holding an open test tube or ignition tube in a flame use a holder of either wood, metal, or paper, the latter folded several times. A rack for holding tubes is shown in Fig. 193.

Drying Tubes.—For drying gases glass tubes called drying tubes, several sorts of which are shown in Fig. 194, are filled with some substance which has affinity for water, as CaCl_2 , pumice stone saturated with H_2SO_4 , etc.

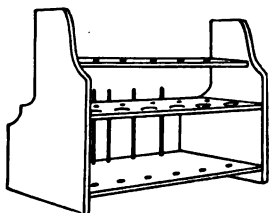


FIG. 193.

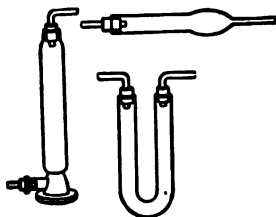


FIG. 194.

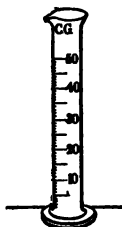


FIG. 195.

Graduates and Burettes.—For measuring liquids cylindrical glasses graduated to cubic centimeters (Fig. 195) are employed. Where great accuracy is necessary, a burette (Fig. 196) takes the place of a graduate. This is a graduated tube drawn to a small bore at one end,

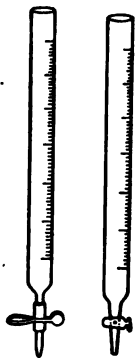


FIG. 196.

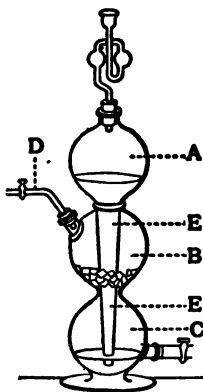


FIG. 197.

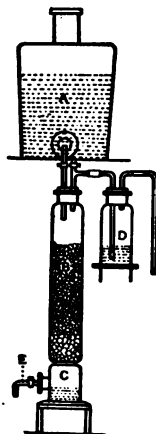


FIG. 198.

over which a rubber tube carrying a pinch-cock can be drawn, or a glass valve may be fitted to the tube. Such arrangements enable the liquid to be drawn out in suitable quantities, even drop by drop.

Gas Generators.—For generating a gas such as H_2S or H , in quantity, Kipp's apparatus (Fig. 197) is well adapted. *A* is a bulb that ends in a long tube, *EE*; *BC* is a double bulb in the upper part of which, *B*, is placed the solid to be acted on, e.g., Zn or FeS . The acid is poured through the thistle tube into *A*, whence it falls to *C*. As soon as it rises to the solid in *B*, gas is liberated and escapes through *D*. When it is desired to check the generation of gas, the valve at *D* is closed, the pressure of the gas in *B* and *C* forces the liquid up into *E* and *A*, and no more gas forms till *D* is again opened.

Another apparatus for producing gas regularly and in any desired quantity is shown in Fig. 198. *A* is a reservoir of dilute acid which falls drop by drop if desired, or in larger quantities on the FeS or other substance in *B*. The gas rises and passes into *D*, where it is washed. The waste liquid collects in *C*, and runs off through *E*.

Bunsen Burners.—A self-adjusting Bunsen burner is a device for regulating the size of the Bunsen flame and at the same time keeping it constantly blue.

Combustion Cup.—A combustion cup or deflagrating spoon may be made by slightly hollowing out the end of an electric-light carbon, or a blackboard crayon, say $1\frac{1}{4}$ " long and winding tightly around it a small copper wire (see p. 23).

ABBREVIATIONS.

app. — apparatus.
 B.B.C.C. — before the blowpipe on charcoal.
 cc — cubic centimeters.
 cm — centimeters.
 cpd. — compound.
 dil. — dilute.
 dis. — dissolve.
 d.t. — delivery tube.
 e.d. — evaporating dish.
 Exp. — experiment.
 g — grams.
 gen. — generator.
 insol. — insoluble.
 i.t. — ignition tube.

N.T.P. — normal temperature and pressure (0° , 760^{cm}).
 ppt. — precipitate.
 p.t. — pneumatic trough.
 cm^2 — square centimeters.
 reagt. — reagent.
 rec. — receiver (wide-mouth bottle).
 r.s. — ring stand.
 sat. — saturate.
 sol. — solution.
 sp. gr. — specific gravity.
 s.r. — stirring rod.
 t.t. — test tube.
 vol. — volume.

COMPLETE LIST OF ELEMENTS.

The following list contains all the 74 elements recognized to date, 1897, with the atomic weights by both $H = 1$ and $O = 16$ standards; it is taken from F. W. Clarke's "Recalculation of the Atomic Weights"; it contains also the discoverer and the date of the isolation of the element.

Several metals of rare earths marked (?) have not yet been isolated.

NAME.	SYM.	H = 1.	O = 16.	DISCOVERY.	DISCOVERER.
Aluminum	Al	26.91	27.11	1827	Wöhler.
Antimony	Sb	119.52	120.43	15th cent.	Valentine.
Argon	A	(?)	(?)	1894	Rayleigh and Ramsay.
Arsenic	As	74.44	75.01	1694	Schröder.
Barium	Ba	136.39	137.43	1808	Davy.
Bismuth	Bi	206.54	208.11	15th cent.	Valentine.
Boron	B	10.86	10.95	1808	Gay Lussac and Thénard.
Bromin	Br	79.34	79.95	1826	Balard.
Cadmium	Cd	111.10	111.95	1817.	Stromeyer.
Calcium	Ca	39.76	40.07	1808	Davy.
Carbon	C	11.92	12.01	Ancient	
Cerium	Ce	139.10	140.20	1826	Mosander.
Cesium	Cs	131.89	132.89	1860	Bunsen.
Chlorin	Cl	35.18	35.45	1774	Scheele.
Chromium	Cr	51.74	52.14	1797	Vauquelin.
Cobalt	Co	58.49	58.93	1742	Brandt.
Columbium	Cb	93.02	93.73	1801	Hatschett.
Copper	Cu	63.12	63.60	Ancient	
Erbium	E	165.06	166.32	(?)	
Fluorin	F	18.91	19.06	1886	Moissan.
Gadolinium	Gd	155.57	156.76	(?)	
Gallium	Ga	69.38	69.91	1875	Boisbaudran.
Germanium	Ge	71.93	72.48	1886	Winkler.
Glucinum	Gl	9.01	9.08	1828	Wöhler.
Gold	Au	195.74	197.23	Ancient	
Helium	He	(?)	(?)	1895	Ramsay.
Hydrogen	H	1	1.008	1766	Cavendish.
Indium	In	112.99	113.85	1863	Reich and Richter.

NAME.	SYM.	H = 1.	O = 16.	DISCOVERY.	DISCOVERER.
Iodin	I	125.89	126.85	1811	Courtois.
Iridium	Ir	191.66	193.12	1804	Tennant.
Iron	Fe	55.60	56.02	Ancient	
Lanthanum	La	137.69	138.64	(?)	Mosander.
Lead	Pb	205.36	206.92	Ancient	
Lithium	Li	6.97	7.03	1817	Arfvedson.
Magnesium	Mg	24.10	24.28	1808	Davy.
Manganese	Mn	54.57	54.99	1774	Gahn.
Mercury	Hg	198.49	200.00	Ancient	
Molybdenum	Mo	95.26	95.99	1782	Hjehu.
Neodymium	Nd	139.70	140.80	(?)	
Nickel	Ni	58.24	58.69	1750	Cronstedt.
Nitrogen	N	13.93	14.04	1772	Rutherford.
Osmium	Os	189.55	190.99	1804	Tennant.
Oxygen	O	15.88	16.00	1774	Priestley.
Palladium	Pd	105.66	106.36	1803	Wollaston.
Phosphorus	P	30.79	31.02	1669	Brand.
Platinum	Pt	193.41	194.89	1750	Watson.
Potassium	K	38.82	39.11	1807	Davy.
Praseodymium	Pr	142.50	143.60	(?)	
Rhodium	Rh	102.23	103.01	1803	Wollaston.
Rubidium	Rb	84.78	85.43	1860	Bunsen.
Ruthenium	Ru	100.91	101.68	1845	Claus.
Samarium	Sm	149.13	150.26	(?)	
Scandium	Sc	43.78	44.12	1879	Nilson.
Selenium	Se	78.42	79.02	1817	Berzelius.
Silicon	Si	28.18	28.40	1822	Berzelius.
Silver	Ag	107.11	107.92	Ancient	
Sodium	Na	22.88	23.05	1807	Davy.
Strontium	Sr	86.95	87.61	1808	Davy.
Sulfur	S	31.83	32.07	Ancient	
Tantalum	Ta	181.45	182.84	1802	Eckeberg.
Tellurium	Te	126.52	127.49	1798	Klaproth.
Terbium	Tr	158.80	160.00	(?)	
Thallium	Tl	202.61	204.15	1862	Crookes.
Thorium	Th	230.87	232.63	1828	Berzelius.
Thulium	Tm	169.40	170.70	(?)	
Tin	Sn	118.15	119.05	Ancient	
Titanium	Ti	47.79	48.15	1824	Berzelius.

NAME.	SYM.	H = 1.	O = 16.	DISCOVERY.	DISCOVERER.
Tungsten	W	183.43	184.83	1785	J. and F. d'Elhujar.
Uranium	U	237.77	239.59	1840	Peligot.
Vanadium	V	50.99	51.38	1867	Roscoe.
Ytterbium	Yt	171.88	173.19	(?)	
Yttrium	Y	88.35	89.02	(?)	Berzelius.
Zinc.....	Zn	64.91	65.41	16th cent.	Paracelsus (?).
Zirconium	Zr	89.72	90.40	1825	Berzelius.

TABLE A. SOLUBILITIES.

Elements.	Acetate.	Arseniate.	Arsenite.	Borate.	Bromid.	Carbonate.	Chlorate.	Chlorid.	Chromate.	Cyanid.	Ferricyanid.	Ferrocyanid.	Fluorid.	Hydroxid.	Iodid.	Nitrate.	Oxalate.	Oxid.	Phosphate.	Silicate.	Sulfate.	Sulfid.
Al ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
NH ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Sb ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Ba ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Bi ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Cd ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Ca ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Cr ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Co ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Cu ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
H ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Fe ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Fe ⁺⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Pb ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Mg ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Mn ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Hg ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Hg ⁺⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Ni ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Ni ⁺⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
K ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Ag ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Na ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Sr ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Sn ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Sn ⁺⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Zn ⁺	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s

S, soluble in water ; s, slightly soluble in water ; I, insoluble in water and acids ; i, insoluble in water, but soluble in acids (HCl, HNO₃, or aqua regia) strong or dilute ; Si, soluble in water with very little acid.

REFERENCE BOOKS.

The following list comprises a few books written in English that are recommended for reference. It is quite desirable that classes should have access to some at least of these works for reference and reading.

BIBLIOGRAPHICAL AND HISTORICAL.

- BOLTON. "Bibliography of Chemistry." 1492-1892. 1212 pages. \$3.50. Chemical Publishing Co., Easton, Pa.
- VON MEYER. "History of Chemistry." 1891. 544 pages. \$4.50. The Macmillan Co., N. Y.
- VENABLE. "History of Chemistry." 1894. 172 pages. \$1.00. D.C. Heath & Co., Boston.

GENERAL AND INDUSTRIAL.

- REMSEN. "Inorganic Chemistry, Advanced Course." 1889. 827 pages. \$2.80. Henry Holt & Co., N. Y.
- BLOXAM. "Inorganic and Organic Chemistry." 1891. 799 pages. \$4.25. P. Blakiston, Son & Co., Phil.
- WATTS. "Fownes' Elementary Chemistry." 1885. 1061 pages. \$2.75. Lea Brothers & Co., Phil.
- SADTLER & TRIMBLE. "Text-Book of Chemistry." 1895. 950 pages. \$5.00. J. B. Lippincott Co., Phil.
- RICHTER. "Inorganic Chemistry." 1891. 432 pages. \$1.75. P. Blakiston, Son & Co., Phil.
- FREER. "General Inorganic Chemistry." 1895. 550 pages. \$3.00. Allyn & Bacon, Boston.
- ROSCOE & SCHORLEMMER. "Treatise on Chemistry." Vols. I and II. 1892. \$11.00. D. Appleton & Co., N. Y.
- REMSEN. "Organic Chemistry." 1885. 374 pages. \$1.20. D. C. Heath & Co., Boston.
- RICHTER. "Organic Chemistry." Revised edition in preparation. P. Blakiston, Son & Co., Phil.
- SADTLER. "Industrial Organic Chemistry." 1891. 519 pages. \$5.00. J. B. Lippincott Co., Phil.
- JOHNSTON. "Chemistry of Common Life." 1891. 592 pages. \$2.00. D. Appleton & Co., N. Y.

- WAGNER. "Chemical Technology." 1888. \$7.50. D. Appleton & Co., N. Y.
- WATTS. "Dictionary of Chemistry." 4 vols. 1892-94. Longmans, Green & Co., N. Y.
- THORPE. "Dictionary of Applied Chemistry." 3 vols. 1894-95. Longmans, Green & Co., N. Y.
- VOGEL. "Chemistry of Light and Photography." \$2.00. D. Appleton & Co., N. Y.

EXPERIMENTAL.

- NEWT. "Chemical Lecture Experiments." 1896. 323 pages. Longmans, Green & Co., N. Y.
- HARCOURT & MADAN. "Practical Chemistry." 1887. 590 pages. \$2.60. D. Van Nostrand Co., N. Y.
- THORP. "Inorganic Chemical Preparations." 1896. 238 pages. \$1.50. Ginn & Co., Boston.
- COMEY. "Dictionary of Solubilities." 1896. 515 pages. \$5.00. The Macmillan Co., N. Y.
- WRIGHT. "Threshold of Science." 1891. 422 pages. \$2.00. J. B. Lippincott Co., Phil.
- PELLEW. "Medical and Physiological Chemistry." 1892. 314 pages. \$2.50. D. Appleton & Co., N. Y.
- COOKE. "Laboratory Practice." 1891. 192 pages. \$1.00. D. Appleton & Co., N. Y.
- WILLIAMS. "Experiments, General and Analytical." 1896. 102 pages. \$0.50. Ginn & Co., Boston.
- WILLIAMS. "Laboratory Manual." 1896. 100 pages. \$0.30. Ginn & Co., Boston.

THEORETICAL.

- APPLETON. "Chemical Philosophy." 1890. 256 pages. \$1.40. Silver, Burdett & Co., Boston.
- REMSEN. "Theoretical Chemistry." 1892. 326 pages. \$2.00. Lea Brothers & Co., Phil.
- COOKE. "New Chemistry." 1884. 400 pages. \$2.00. D. Appleton & Co., N. Y.
- WURTZ. "The Atomic Theory." \$1.50. D. Appleton & Co., N. Y.
- COOKE. "Chemical Philosophy." 1891. 623 pages. \$3.50. Allyn & Bacon, Boston.
- RISTEEN. "Molecules and the Molecular Theory." 1895. 223 pages. \$2.00. Ginn & Co., Boston.

OSTWALD. "Scientific Foundations of Analytical Chemistry." 1894. 207 pages. The Macmillan Co., N. Y.

ANALYTICAL.

MENSCHUTKIN. "Analytical Chemistry." 1895. 293 pages. \$4.00. The Macmillan Co., N. Y.

NOYES. "Qualitative Analysis." 1896. 89 pages. \$1.25. The Macmillan Co., N. Y.

PRESCOTT & JOHNSTON. "Qualitative Analysis." 1888. 317 pages. \$3.50. D. Van Nostrand Co., N. Y.

FRESENIUS. "Qualitative Analysis." 1883. 500 pages. \$4.00. John Wiley & Sons, N. Y.

WILLIAMS. "Experiments, General and Analytical." 1896. 102 pages. \$0.50. Ginn & Co., Boston.

PHYSIOLOGICAL.

FOSTER. "Chemical Basis of Animal Body." \$1.75. The Macmillan Co., N. Y.

HALLIBURTON. "Essentials of Chemical Physiology." 1896. \$1.50. Longmans, Green & Co., N. Y.

GAMGEE. "Chemistry of the Animal Body." 2 vols. \$9.00. The Macmillan Co., N. Y.

TANNER. "Memoranda of Poisons." \$0.75. P. Blakiston, Son & Co., Phil.

SCHUTZENBERGER. "Fermentation." 1886. 331 pages. \$1.50. D. Appleton & Co., N. Y.

WILLIAMS. "The Chemistry of Cookery." \$1.50. D. Appleton & Co., N. Y.

ABBOT. "Principles of Bacteriology." \$2.50. Chemical Publishing Co., Easton, Pa.

SOLUTIONS.

For solutions to be used in analysis substances should be C.P., and dissolved in distilled water, the solutions filtered if necessary, and put into, *e.g.*, 500^{cc} bottles placed on convenient shelves for class use. For general reactions commercial compounds may be used. Solutions for some of the more important solids are given below. Others may be made by mixing say 50^{cc} with 500^{cc} of H₂O and filtering. Some few should be saturated.

NUMBER OF GRAMS OF SOLIDS TO 500^{cc} H₂O.

Acids, etc. (a)	HgCl ₂ 25	Na ₂ SO ₃100
AgNO ₃ 25 (b)	HgNO ₃ 25 (g)	NH ₄ Cl 60
AlCl ₃ 50	KBr 25	(NH ₄) ₂ CO ₃125
AsCl ₃ (c)	KCN..... 50	(NH ₄) ₂ C ₂ O ₄ 20
BaCl ₂ 50	KCl..... 25	NH ₄ NO ₃ 50
BiCl ₃ (d)	K ₂ CrO ₄ 25	(NH ₄) ₂ S (h)
C ₁₂ H ₂₂ O ₁₁ sat.	K ₂ Cr ₂ O ₇ 25	(NH ₄) ₂ S _x (h)
CaCl ₂ 50	K ₄ Fe(CN) ₆ 40	(NH ₄) ₂ SO ₄ 5 (i)
Ca(OH) ₂ sat.	KI..... 25	NiCl ₂ 25
CaSO ₄ " (e)	KNO ₂ 50	Pb(C ₂ H ₃ O ₂) ₂ 50
CdCl ₂ 25	KNO ₃ 50	PbCl ₂ sat.
CoCl ₂ 25	KOH 60	Pb(NO ₃) ₂ 50
CrCl ₃ 25 (f)	MgCl ₂ 50	PtCl ₄ (j)
CuCl ₂ 25	MgSO ₄ 50	SnCl ₂ 40 (k)
Cu(NO ₃) ₂ 25	MnCl ₂ 25	SrCl ₂ 50
FeCl ₃ 25	Na ₂ AsO ₃ 25 (c)	SbCl ₃ (l)
FeSO ₄ 50 (e)	NaCl..... 50	ZnCl ₂ 25
HNaCO ₃ 50	Na ₂ CO ₃ 50	
HNa ₂ PO ₄ 50	NaOH 60	

(a) Use the concentrated acids unless dilute (dil.) are mentioned. Dilute acids (HCl, HNO₃, H₂SO₄) are prepared by adding one volume of concentrated acid to four volumes of water. NH₄OH (if of 26°) should be diluted with three times its volume of water.

(b) AgNO₃ sol. should not be filtered, nor brought in contact with any organic substance which tends to break it up.

(c) AsCl₃ sol. may be prepared by adding H₂O to Na₂AsO₃, then adding HCl till effervescence stops.

(d) Prepare BiCl_3 sol. by adding H_2O to bismuth oxychlorid, BiOCl , then stirring into it HCl . Not a great quantity will dissolve.

(e) Some substances decompose, oxidize, or precipitate when left in solution, and these should be prepared only as wanted.

(f) CrCl_3 may be prepared as follows, as the crystalline variety is rather expensive: To some $\text{K}_2\text{Cr}_2\text{O}_7$ sol., add some HCl (say $\frac{1}{10}$) and a little alcohol. Stir well, boil for some time, then let it stand, when the color changes from red to green, and CrCl_3 is formed.

(g) Dissolve 25g of HgNO_3 crystals in a mixture of 475cc of H_2O and 25cc of HNO_3 . Or it may be made by pouring dil. HNO_3 on more Hg than will dissolve and leaving it in a warm place for 24 hours. A little metallic mercury should be left in the bottom of the bottle.

(h) $(\text{NH}_4)_2\text{S}$. Dilute NH_4OH (a), then pass H_2S into 300cc of it until it is saturated, then add 200cc of NH_4OH (diluted as before). There is first formed $(\text{NH}_4)_2\text{S}$ (colorless), then $(\text{NH}_4)_2\text{SH}$ (yellow). Adding NH_4OH forms $(\text{NH}_4)_2\text{S}$. Ammonium polysulfid, $(\text{NH}_4)_2\text{S}_x$, is made by stirring $(\text{NH}_4)_2\text{S}$ for some time with flowers of sulfur, then filtering.

(i) $(\text{NH}_4)_2\text{SO}_4$ sol. when used to separate Sr from Ca must be very dilute so as not to precipitate Ca . The strength of the $(\text{NH}_4)_2\text{SO}_4$ solution depends upon the strength of the Ca solution.

(j) This reagent is very expensive, and is best bought in solution already prepared.

(k) SnCl_2 forms a basic salt with water alone. Hence the solution must be acidified with considerable HCl . It easily oxidizes, and so pieces of metallic Sn should be kept in the bottle. Even then solutions will not remain very long intact, and they must be made reasonably fresh.

(l) Add a little butter of antimony, SbCl_3 , to water well acidified with HCl , as SbCl_3 with H_2O forms SbOCl , which is insoluble.

Cochineal Solution. Grind up a handful of cochineal in a mortar, add water, stir, and filter it.

Litmus Solution. Pulverize litmus cubes, add water, and filter the solution.

Indigo Solution. (Sulfindigotic acid.) Slowly mix and stir 5g pulverized indigo with 25cc H_2SO_4 (or $\text{H}_2\text{S}_2\text{O}_7$, fuming sulfuric acid) in a beaker immersed in cold water. Cover the beaker, and after 48 hours add 500cc H_2O , stir, and filter.

INDIVIDUAL APPARATUS.

The author has selected apparatus specially adapted, as to exact dimensions, quality, and cheapness, for performing in the best way the experiments herein described, and sets or separate pieces of this, together with other apparatus and chemicals, can be had of the Ziegler Electric Co., 141 Franklin St., Boston, to which firm teachers are referred for catalogs.

- | | |
|--|--|
| 4 re-agent bottles, 250 cc. glass stoppers, blown labels: NH_4OH , HCl , HNO_3 , H_2SO_4 . | 1 camel's-hair brush. |
| 1 pneumatic trough. | 1 magnet. |
| 1 Hessian crucible. | 4 wide-mouthed bottles. |
| 2 beakers. | 1 2-holed rubber stopper to fit above. |
| 2 pieces wire gauze. | 4 pieces window-glass. |
| 1 piece platinum wire. | 1 glass funnel. |
| 1 mouth blowpipe. | 1 porcelain evap. dish. |
| 6 pieces glass tubing. | 1 asbestos board. |
| 4 pieces hard glass tubing. | 1 sand bath. |
| 1 test-tube brush. | 1 pair iron forceps. |
| 1 small tube brush. | 1 triangular file. |
| 1 doz. test tubes. | 1 round file. |
| 4 cork stoppers, for tubes. | 1 piece copper wire. |
| 1 fish-tail attachment for Bunsen burner. | 1 piece lead wire. |
| 1 burner tube with rest for blowpipe. | 1 piece zinc wire. |
| 1 piece sheet copper. | 1 wooden test-tube holder. |
| 1 glass retort. | 1 wire test-tube rack. |
| 1 tumbler. | 1 thistle tube. |
| 1 piece cobalt glass. | 1 Bohemian flask. |
| 1 horn spatula. | 1 2-holed rubber stopper to fit flask. |
| 1 sheet litmus paper. | 1 Bunsen burner. |
| 200 filter papers. | 1 iron ring stand. |
| 1 bunch splints. | 2 ft. rubber tubing. |
| 1 sheet turmeric paper. | 1 ft. " " |
| | 1 metric ruler. |
| | 1 graduate. |
| | 1 small leaden dish. |

GENERAL APPARATUS.

The requirements of general apparatus for a laboratory are too numerous and varied to be given here. A few of the pieces in more general demand for experiments in this book are as follows:

Glass-stoppered bottles.	Filter-stands.
Graduates.	Glass and rubber tubing.
Funnels.	Steel glass-cutters.
Fruit jars (for making solutions).	Steel wire-cutters.
Scales, with metric weights.	Mortars and pestles.
Ignition tubes.	Flasks.
Beakers.	Filter papers, etc., etc.

CHEMICALS.

The following is a list of chemicals sufficient to perform the more important experiments described in this book. The estimate is made for a class of 20 students.

Acid, acetic, $\text{HC}_2\text{H}_3\text{O}_2$	4 lb.	Arsenopyrite, FeAsS	$\frac{1}{2}$ lb.
“ boric, H_3BO_3	$\frac{1}{2}$ “	Barium chlorid, BaCl_2	$\frac{1}{2}$ “
“ hydrochloric, HCl	25 “	“ hydroxid, $\text{Ba}(\text{OH})_2$	$\frac{1}{2}$ “
“ hydrofluoric, HF	$\frac{1}{2}$ “	Bismuth oxychlorid, BiOCl	$\frac{1}{2}$ “
“ hydrofluosilicic, H_2SiF_6	$\frac{1}{2}$ “	Calcium chlorid, CaCl_2	$\frac{1}{2}$ “
“ nitric, HNO_3	12 “	“ fluorid, powdered, CaF_2	$\frac{1}{2}$ “
“ oxalic, $\text{H}_2\text{C}_2\text{O}_4$	$\frac{1}{2}$ “	“ hypochlorite, CaCl_2O	$\frac{1}{2}$ “
“ phosphoric, H_3PO_4	$\frac{1}{2}$ “	“ sulfate, CaSO_4	$\frac{1}{2}$ “
“ sulfuric, H_2SO_4	18 “	“ oxid, CaO	2 “
“ tartaric, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	$\frac{1}{2}$ “	Carbon bisulfid, CS_2	$\frac{1}{2}$ “
Alcohol, $\text{C}_2\text{H}_5\text{OH}$	1 qt.	Charcoal, animal, gran., C	1 “
Alum, $\text{K}_2\text{Al}_2(\text{SO}_4)_4$	1 lb.	“ “ powdered, C	1 “
Aluminum chlorid, AlCl_3	$\frac{1}{2}$ “	“ wood, “ C	1 “
Ammonium carbon., $(\text{NH}_4)_2\text{CO}_3$	1 “	“ “ C	20 pieces
“ chlorid, NH_4Cl	2 “	Cobalt chlorid, CoCl_2	$\frac{1}{2}$ lb.
“ hydroxid, NH_4OH	20 “	“ nitrate, $\text{Co}(\text{NO}_3)_2$	$\frac{1}{2}$ “
“ nitrate, NH_4NO_3	1 “	Cochineal.....	$\frac{1}{2}$ “
“ oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4$	$\frac{1}{2}$ “	Copper, turnings, Cu	3 “
“ sulfate, $(\text{NH}_4)_2\text{SO}_4$	$\frac{1}{2}$ “	“ sheet, Cu	$\frac{1}{2}$ “
Antimony cryst., Sb	$\frac{1}{2}$ “	“ chlorid, CuCl_2	1 “
“ chlorid, SbCl_3	$\frac{1}{2}$ “	“ nitrate, $\text{Cu}(\text{NO}_3)_2$	$\frac{1}{2}$ “
Arsenious oxid, As_4O_6	1 oz.	“ oxid, CuO	1 “

Copper sulfate, CuSO_4	$\frac{1}{2}$ lb.	Potassium cyanid, KCN	$\frac{1}{2}$ lb.
Ether, $(\text{C}_2\text{H}_5)_2\text{O}$	$\frac{1}{2}$ "	" dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$	1 "
Gold leaf, Au	1 bk.	" ferrocyan., $\text{K}_4\text{Fe}(\text{CN})_6$	1 "
Indigo	$\frac{1}{2}$ lb.	" ferricy., $\text{K}_3\text{Fe}(\text{CN})_6$	$\frac{2}{3}$ "
Iodin, I	2 oz.	" iodid, KI	1 "
Iron, fine turnings, Fe	1 lb.	" hydroxid, KOH	1 "
" by hydrogen, Fe	$\frac{1}{2}$ "	" nitrate, KNO_3	1 "
" perchlorid, FeCl_3	1 "	" nitrite, KNO_2	$\frac{1}{2}$ "
" protosulfid, FeS	5 "	" permangan., KMnO_4	$\frac{1}{2}$ "
" pyrite, FeS_2	$\frac{1}{2}$ "	" sulfocyanid, KSCN	$\frac{1}{2}$ "
" sulfate, FeSO_4	1 "	" tarttrate, $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$	$\frac{1}{2}$ "
Lead, sheet, Pb	1 "	Silica, powdered, SiO_2	$\frac{1}{2}$ "
" wire, $\frac{1}{8}$ in. diam., Pb	12 ft.	Silver nitrate, AgNO_3	4 oz.
" acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$	$\frac{1}{2}$ lb.	Sodium, metallic, Na	$\frac{1}{2}$ "
" chlorid, PbCl_2	$\frac{1}{2}$ "	" acetate, $\text{NaC}_2\text{H}_3\text{O}_2$	$\frac{1}{2}$ lb.
" nitrate, $\text{Pb}(\text{NO}_3)_2$	2 "	" arsenite, HNa_2AsO_3	$\frac{1}{2}$ "
" protoxid, PbO	$\frac{1}{2}$ "	" bicarbonate, HNaCO_3	$\frac{1}{2}$ "
" tetroxid (red), Pb_3O_4	$\frac{1}{2}$ "	" bisulfate, HNaSO_4	$\frac{1}{2}$ "
Litmus, cubes	1 oz.	" borate, $\text{Na}_2\text{B}_4\text{O}_7$	$\frac{1}{2}$ "
" paper	$\frac{1}{2}$ quire	" carbonate, Na_2CO_3	3 "
Marble chips, CaCO_3	3 lb.	" chlorid, NaCl	4 "
Magnesium ribbon, Mg	10 ft.	" hydroxid (caust.), NaOH	3 "
" chlorid, MgCl_2	$\frac{1}{2}$ lb.	" nitrate, NaNO_3	2 "
" sulfate, MgSO_4	$\frac{1}{2}$ "	" nitrite, NaNO_2	$\frac{1}{2}$ "
Manganese chlorid, MnCl_2	$\frac{1}{2}$ "	" oxalate, $\text{Na}_2\text{C}_2\text{O}_4$	$\frac{1}{2}$ "
" dioxid, gran., MnO_2	$\frac{1}{2}$ "	" phosphate, HNa_2PO_4	1 "
" powd., MnO_2	$1\frac{1}{2}$ "	" sulfate, Na_2SO_4	1 "
Mercury, Hg	$\frac{1}{2}$ "	" sulfid, Na_2S	$\frac{1}{2}$ "
" bichlorid, HgCl_2	$\frac{2}{3}$ "	" sulfite, Na_2SO_3	$\frac{1}{2}$ "
" protochlorid, HgCl	$\frac{1}{2}$ "	" thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$	1 "
" pernitrate, $\text{Hg}(\text{NO}_3)_2$	$\frac{1}{2}$ "	Starch, $\text{C}_6\text{H}_{10}\text{O}_5$	$\frac{1}{2}$ "
" protonitrate, HgNO_3	$\frac{1}{2}$ "	Strontium chlorid, SrCl_2	$\frac{1}{2}$ "
" oxid, HgO	1 "	Sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$	1 "
Nessler's sol.	$\frac{1}{2}$ "	Sulfur, brimstone, S	2 "
Phosphorus, P	2 oz.	" flowers, S	1 "
Picture wire	1 roll	Tin bichlorid, SnCl_2	$\frac{1}{2}$ "
Platinum chlorid sol., H_2PtCl_6	1 oz.	Turmeric paper	1 sheet
Potassium, metallic, K	$\frac{1}{2}$ "	Turpentine, $\text{C}_{10}\text{H}_{18}$	1 oz.
" bromid, KBr	$\frac{1}{2}$ lb.	Zinc, gran., Zn	3 lb.
" carbonate, K_2CO_3	$1\frac{1}{2}$ "	" wire, $\frac{1}{8}$ in. diam.	12 ft.
" chlorid, KI	$\frac{2}{3}$ "	" (arsenic-free)	1 lb.
" chlorate, KClO_3	2 "	" chlorid, ZnCl_2	$\frac{1}{2}$ "
" chromate, K_2CrO_4	$\frac{1}{2}$ "	" nitrate, $\text{Zn}(\text{NO}_3)_2$	$\frac{1}{2}$ "

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